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Nickel(II) in Molten Nitrate Eutectics Containing Added Chloride. Identification of Complexes, Equilibria and Terminal Spectra, and Determination of Enthalpy Values by a New Computer-Based Procedure

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The electronic spectrum of nickel(II) in the molten eutectics $NaNO_3$–KNO_3 and $LiNO_3$–$NaNO_3$–KNO_3 with added chloride, from pure nitrate to pure chloride, was examined over a wide temperature range. The spectroscopic behavior was divided into five chloride concentration ranges. The species $Ni(NO_3)_3^-$, $NiCl(NO_3)_3^{2-}$, and $NiCl_2(NO_3)_x^{x-}$, where $x = 2$ or 3, $NiCl_3(NO_3)^{2-}$, $NiCl_5(NO_3)$, and $NiCl_6$ were found and, excepting the latter two, were readily identified as complexes rather than centers. Various two-species equilibria predominated at different chloride concentrations, and when the temperature-dependent spectra were found to be internally linear, the terminal spectra of the component species were generated. The relationship between the equilibrium quotient, K_R', and β, the internal linearity constant, is derived and hence ΔH for the various equilibria calculated. The enthalpy values were lower than any previously obtained for equilibria involving chloronickel complexes and this and the special effects evinced by the lithium cation are discussed.

Introduction

In recent years, research in this laboratory has been directed toward elucidating the chloro complexes of nickel(II) formed in various solvents including water,[1] acetone and dimethyl sulfone,[2] ethylene glycol and glycerol,[3] and dimethyl sulfoxide.[4] These investigations studied the effect of temperature and chloride concentration on the spectra of such solutions; various octahedral and tetrahedral nickel(II) complexes were identified, and the enthalpy values of octahedral–tetrahedral equilibria often obtained. The complexes of nickel(II) in fused nitrate eutectics are invariably octahedral,[5–7] but in molten chlorides and chloride eutectics tetrahedral, and distorted tetrahedral, $NiCl_4^{2-}$ species are generally found.[8–10] To our knowledge, only one paper has appeared which includes a preliminary account of the effect of added chloride on the spectrum of nickel(II) in a nitrate melt.[5] The current investigation was therefore initiated, employing other eutectic mixtures, and the number and nature of the nickel complexes formed in mixed alkali chloride and nitrate melts, over a wide temperature and composition range, are here reported. The formation of these complexes as a function of the cations present in the melts and their stability over ranges of both temperature and composition have also been studied. Previous workers[8,11] have performed certain computer calculations on digitized spectra obtained from chloride melts and we have extended this approach, and, applying the concept of internal linearity,[12] have derived a relationship with the enthalpy value for temperature-dependent reactions. Acceptable ΔH values were computed by this new procedure and they were lower than any found previously for equilibria involving chloronickel(II) species.

Experimental Section

Materials. Experiments involving molten salts require anhydrous materials, and molten nitrates are good oxidizing agents, particularly at high temperatures and with catalytic amounts of water present. The oxidation of some nickel(II) solutions was observed, after a few hours, but this was kept to a minimum by rigorous drying of the starting materials.

Two nitrate eutectics were employed, a binary mixture, $NaNO_3$–KNO_3, 45–55 mol %, and a ternary mixture, $LiNO_3$–$NaNO_3$–KNO_3, 37.5–18.0–44.5 mol %, and two drying techniques were used, oven drying and preelectrolysis. The apparatus used in this latter technique is shown in Figure 1. The Pyrex outer tube may be heated electrically to 500°, and when the ground-glass ends were sealed with water-cooled brass plates fitted with O rings, the cell could be evacuated. The potential between the electrodes was set at 1 V, and after evacuation, the melt was electrolyzed for 10 hr. Under a pressure of 10^{-3}–10^{-4} mm, the initial current of 200×10^{-6} A fell to less than 20×10^{-6} A. The constant potential of 1 V was sufficient to remove traces of water and some heavy metals from the melt without discharging nitrate ions.[13] When preelectrolysis was completed, the bulb blown onto the end of the inner tube was punctured with the glass rod and the melt was filtered through the sintered-glass frit, under pressure from dry nitrogen led into the top of the cell. After solidifying under vacuum the eutectic was stored in a drybox.

The preelectrolysis technique was found to be comparable with normal oven-drying methods for removing water from this eutectic; it also permits the discharge of other impurities from the melt (indicated by the fall in electrode current) and homogenizes the components on fusion of the mixture.

The ternary nitrate eutectic (lithium nitrate from Alfa Inorganics Inc.) was preelectrolyzed as preelectrolysis is one of the few satisfactory methods for drying lithium nitrate. On fusion a yellow-brown solution formed, due to oxidation of trace amounts of the organic solvent from which lithium nitrate was commercially recrystallized. The coloration faded as the melt was electrolyzed. The electrolysis was terminated after 30 hr, to prevent buildup of decomposition products.[14] The moisture content of the solidified eutectic was found to be 0.10%.

The binary and ternary chloride mixtures were prepared with the same cation ratios as the nitrate eutectics, so that this ratio would remain constant as chloride was added to nitrate melts. Preelectrolysis was not possible with the binary NaCl–KCl mixture, as its melting point was above the softening point of Pyrex. Details of the eutectics and mixtures are given in Table I.

The major impurity expected in the nitrate eutectics is the nitrite ion. The standard nitrite determination requires the addition of excess permanganate to the nitrite solution followed by a back-titration with standard iron(II) solution. At the low concentrations involved here it was not possible to detect accurately the pink to colorless end point. The titration scheme was therefore modified to involve a double back-titration. Excess iron(II) solution was added to the nitrite–permanganate mixture which was then back-titrated with more standardized permanganate solution, and the end point was then more easily detected. As supplied, the individual nitrates were found to contain between 0.001 and 0.004% by weight of nitrite, and after preelectrolysis this value increased to around 0.017%. The nitrite level increased as the length of time and the temperature of the melt were increased but did not exceed 0.05% in any of the samples analyzed.

Anhydrous nickel chloride, prepared from the elements and sublimed under vacuum, was kindly donated by Dr. G. P. Smith, Oak Ridge National Laboratory, Oak Ridge, Tenn. Nickel nitrate, as $Ni(NO_3)_2 \cdot 6H_2O$, Fisons analytical reagent, was used without further purification. Attempts to prepare the anhydrous material, in liquid dinitrogen tetroxide, were unsuccessful, the product decomposing before all the solvent was removed. The hydrated salt was used only for experiments in pure nitrate melts and only for cases where chloride:nickel mole ratios of less than 2 were required.

Preparation of Melts. The nitrate eutectics and the chloride mixtures were stored in containers with screw lids in a large drybox maintained at around 50 ppm moisture, monitored by a Series 1000 indicating hygrometer (Moisture Control and Measurement Ltd., Boston Spa, Yorkshire, England). Molten salt solutions were prepared by weighing (to 10^{-3} g) in the drybox the appropriate amount of eutectic, and chloride, into a cell. When it was in the furnace, a slow stream of dried, oxygen-free nitrogen was passed through the cell.

Table I. Salt Mixtures Dried by Preelectrolysis

Salt mixture	Compn, mol %	Mp, °C	Electrode current, A × 10^6 Initial	Electrode current, A × 10^6 Final	Time, hr	Temp, °C
$NaNO_3$-KNO_3	45-55[a]	222[b]	111	24	7	300
NaCl-KCl	45-55		Heated under vacuum		6	500
	50-50[a]	658[c]				
$LiNO_3$-$NaNO_3$-KNO_3	37.5-18.0-44.5[a]	120[d]	150	110	30	200
LiCl-NaCl-KCl	37.5-18.0-44.5	490	180	9.7	11	500
	55-9-36[a]	346[e]				

[a] Eutectic compositions. [b] A. Kofler, *Monatsh. Chem.*, 86, 646 (1955). [c] G. J. Janz, "Molten Salts Handbook," Academic Press, New York, N.Y., 1967, p 34. [d] A. G. Bergman and K. Nogoev, *Russ. J. Inorg. Chem.*, 9, 771 (1964). [e] E. K. Akopov and A. G. Bergman, *ibid.*, 11, 937 (1966).

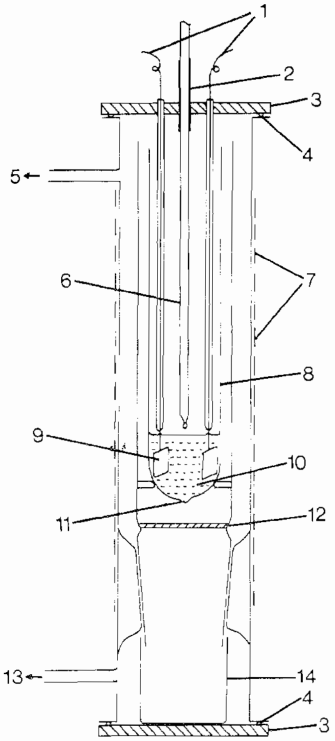

Figure 1. Apparatus for preelectrolyzing molten salts: 1, Ag wire, applied potential 1 V; 2, sliding ground-glass seal; 3, brass sealing plate; 4, O ring; 5, to vacuum, also nitrogen inlet; 6, pointed glass rod; 7, insulated heating elements; 8, Pyrex container; 9, platinum electrodes; 10, fused salt; 11, glass bulb; 12, sintered-glass frit; 13, to vacuum; 14, beaker.

Table II. Densities of Solvents

Solvent and mol % compn	A,[a] g cm^{-3}	10^3B, g cm^{-3} deg^{-1}	T range, °C	Source
$NaNO_3$-KNO_3				
45-55	2.122	0.765	250-550	*b*
47-53	2.290	1.33	270-400	*c*
40-60	2.119	0.723	242-452	*d*
50-50	2.122	0.720	252-455	*d*
NaCl-KCl				
41-59	1.977	0.575	685-908	*e*
51.23-48.77	1.976	0.568	670-909	*e*
$LiNO_3$-$NaNO_3$-KNO_3				
37.5-18.0-44.5	2.077	0.824	120-240	*f*
	2.046	0.690	250-410	*f*
	2.086	0.753	Not quoted	*g*
LiCl-NaCl-KCl				
37.5-18.0-44.5	1.918	0.550	495-530	*f*

[a] Density = $A - BT$, where T is temperature in °C. [b] L. G. Boxall and K. E. Johnson, *J. Chem. Eng. Data*, 16, 204 (1971). [c] P. C. Papaioannou and G. W. Harrington, *J. Phys. Chem.*, 68, 2424 (1964). [d] Fitted to the data of K. Laybourn and W. M. Madgin, *J. Chem. Soc.*, 1 (1934). [e] E. R. van Artsdalen and I. S. Yaffe, *J. Phys. Chem.*, 59, 118 (1955). [f] This work. [g] Reference 7.

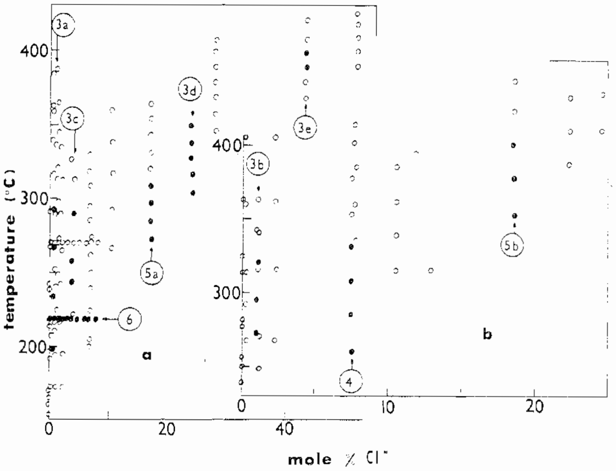

Figure 2. Experimental situations investigated: (a) ternary nitrate melt; (b) binary nitrate melt; solid circles denote the spectra shown here in figures, indicated by numbers and arrows.

To avoid difficulties with electrostatic charges when adding nickel chloride, pellets of this material were made in a hand press, broken into suitable sizes, and transferred as required into a small stoppered bottle which was then weighed, outside the drybox, to 10^{-5} g. This led to accurate molar absorbances, but the reduced surface area mitigated against rapid solution.

Spectrophotometric Measurements. All spectra were recorded on a Cary 14H spectrophotometer, with air as reference, using a ceramic tube furnace for measurements above 400°. This furnace was based on a design by Boston and Smith[15] but with the modifications and power regulation described by Griffiths and Scarrow;[1] for temperatures below 400° an aluminum block furnace[16] was used. A prerecorded (appropriate) base line spectrum was subtracted from all sample spectra.

Initially the spectra were digitized manually from the original charts at 5-nm intervals of wavelength, but subsequently digitizing equipment (Harrison Instruments Ltd., Farnborough, Hampshire, England) was interfaced, (technical details will be published elsewhere). Automatically digitized spectra were recorded at 1-nm intervals.

Density Measurements. Measurements were made using essentially the apparatus described by Griffiths,[17] and densities were calculated from the variation in buoyancy with temperature of a bicone platinum bob suspended in the various melts. The results are given and compared with other data in Table II. Two values are given for the ternary nitrate eutectic as the data fitted two straight lines intersecting at 245°. This anomaly may have resulted from slight decomposition at the higher temperatures or from surface tension effects.

The spectra of all solutions studied were corrected for the thermal expansion of solutions, using the density data given in Table II. As the concentration of nickel rarely exceeded 10^{-2} M, its effect was assumed negligible. When large concentrations of chloride were added to the nitrate eutectics, an approximation was used; it was assumed that the added chloride had the same density as the solvent: molar volumes for molten salt mixtures are frequently additive.[18]

Results

The range of compositions and temperatures over which spectra were recorded for the binary and ternary systems is shown in Figure 2: those reported here are indicated.

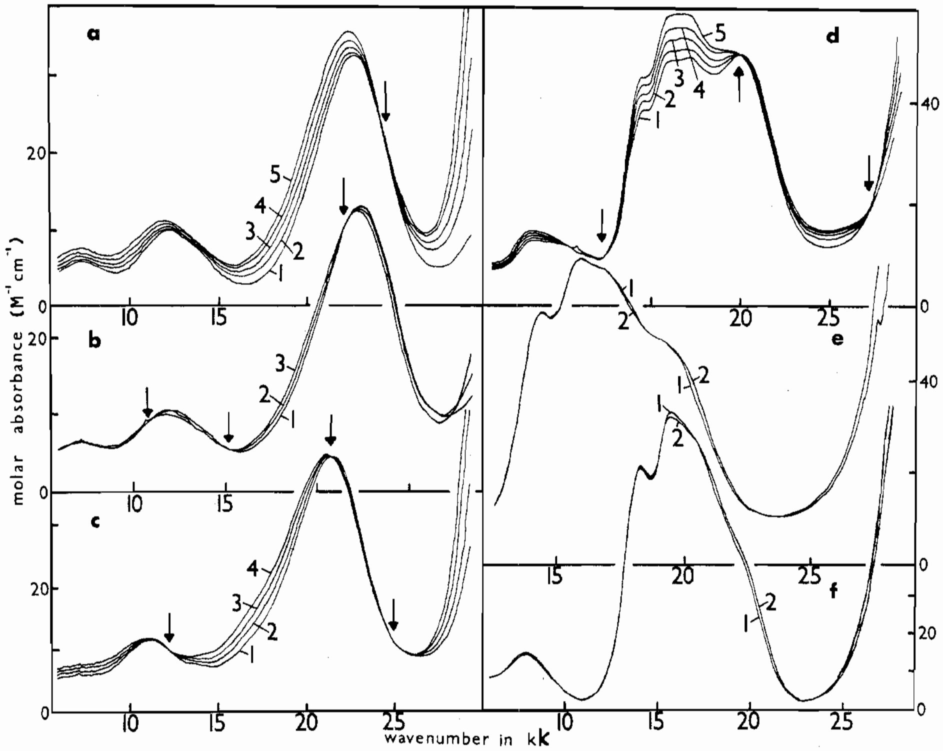

Figure 3. Effect of temperature of the spectrum of nickel(II) in nitrate melts with added chloride. Arrows show positions of isosbestic points. (a) Ternary melt + 0.956 mol % Cl^-: (1) 197°, (2) 219°, (3) 233°, (4) 267°, (5) 291°; absorbance of spectrum (1) increased empirically by 3.9% (to correct for slow dissolution of $NiCl_2$) and that of spectrum (5) by 4.2% (correction for onset of decomposition). (b) Binary melt + 1.16 mol % Cl^-: (1) 271°, (2) 295°, (3) 319°. (c) Ternary melt + 3.93 mol % Cl^-: (1) 220°, (2) 242°, (3) 256°, (4) 289°. (d) Ternary melt + 24.26 mol % Cl^-: (1) 302°, (2) 314°, (3) 325°, (4) 336°, (5) 347°; absorbance of spectrum (5) increased by 1.1% to correct for onset of decomposition. (e) Ternary melt + 43.76 mol % Cl^-: (1) 387°, (2) 397°; band profile changed little in the range 366–419°. (f) Ternary melt of pure LiCl-NaCl-KCl: (1) 553°, (2) 573°.

Decomposition of Melts and Its Correction. All solutions of nickel(II) in mixed nitrate melts decomposed eventually. The time interval before deterioration was detected, and considered unacceptable, varied: it was lengthened by moderate concentrations of chloride ions and shortened on raising the temperature. The ternary melts decomposed more slowly than the binary melts.

Melts containing more than 5 mol % chloride, even though a slow stream of purified nitrogen was present, ultimately deposited brown particles. Brough and Kerridge[19] have analyzed a golden-brown precipitate, from nickel chloride solutions in $LiNO_3$–KNO_3 eutectic at 160°, and suggested the species $(LiK)_2NiCl_2(NO_3)_2$. The precipitate observed here is associated with oxidation products of nickel(II), particularly since the addition of small quantities of ammonium nitrate, acting as a Lewis acid, redissolved the precipitate. Decomposition was observed spectroscopically by a small decrease in the intensity of spectra.

Decomposition of solutions containing less than 5 mol % chloride, when this occurred, gave a dark yellow-green deposit on the surface of melts. These melts had a high viscosity just above their melting points, and even with agitation, nickel chloride took a long time to dissolve, leaving little time for acceptable spectroscopic measurements.

The careful drying procedures lengthened the stable situation to 2–3 hr for most melts. Subsequent examination of spectra meant that over 50% had to be discarded due to the onset of decomposition. A few spectra, recorded when the onset had caused only a small change in absorbance, are included in the figures. The intensity of these spectra was increased by an empirical factor which never caused an absorbance change of more than 3%. On such occasions, the corrected spectrum was found to pass through the isosbestic points defined by at least three uncorrected spectra. The few empirically corrected spectra illustrated here are labeled as such.

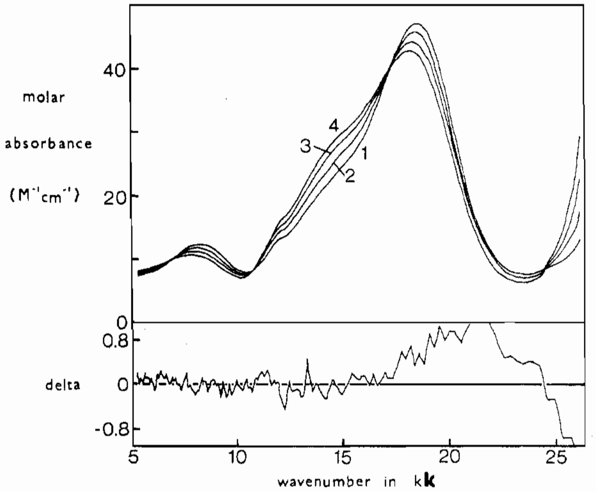

Figure 4. Effect of temperature on spectrum of $NiCl_2$ (0.079 *M*) in a binary nitrate melt containing 7.55 mol % Cl^-: (1) 259°, (2) 284°, (3) 307°, (4) 330°; internal linearity function delta (Δ) calculated for spectrum (4) relative to spectra (3) and (1) from a β value of 1.393; root-mean-square deviation of $\Delta = 0.045\ M^{-1}\ cm^{-1}$.

Effect of Temperature on the Spectra of Melts at Constant Composition. The spectrum of nickel(II) in nitrate melts of composition 0–100% chloride was recorded and an identical sequence of changes was observed for both the binary and ternary melts with temperature increase. Examples are illustrated from both systems in Figures 3–5. The temperature dependence varied with melt composition and five types of behavior are distinguished. The changeover composition is not the same for binary and ternary melts and is summarized in Table III.

Range A. It will later be shown that nickel forms only octahedral complexes in solutions within this composition range.

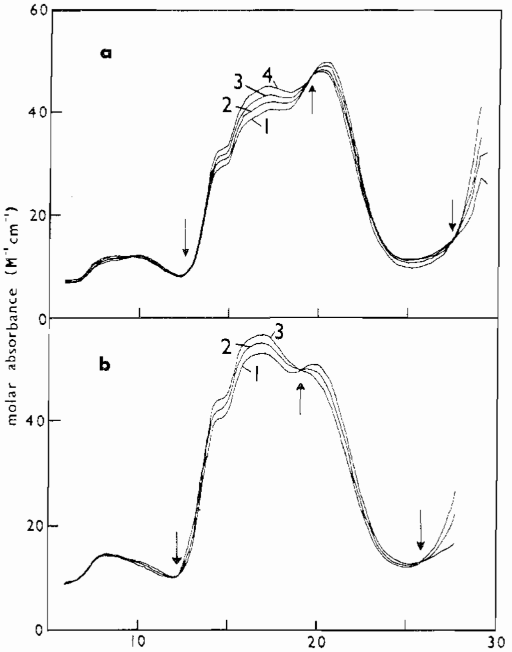

Figure 5. (a) Ternary melt + 17.25 mol % Cl⁻: spectrum of $NiCl_2$ (0.082 *M*) recorded at (1) 272°, (2) 283°, (3) 295°, and (4) 307°; absorbance of spectrum (4) increased by 2.5% to correct for decomposition. (b) Binary melt + 18.46 mol % Cl⁻: spectrum of $NiCl_2$ (0.073 *M*) recorded at (1) 355°, (2) 377°, and (3) 400°; arrows indicate positions of isosbestic points.

Table III

Compn range	Mol % Cl⁻	
	Binary melt	Ternary melt
A	0.0-1.1	0.0-1.2
B	1.1-3.5	1.2-2.0
C	3.5-7.0	2.0-6.0
D	7.0-25	6.0-22
E	25-100	22-100

With temperature increase, an increase in this octahedral spectrum is observed at all wavelengths (Figure 3a). The 12.0-kK band is weakly split into two components.

Range B. Temperature has a small but regular effect on spectra recorded in this composition range (Figure 3b). Isosbestic points are observed at about 27.0, 21.7, 15.4, and 11.1 kK. The splitting of the octahedral 12.0-kK band is now almost undetectable and there is no evidence of tetrahedral absorption bands in this range.

Range C. In this region temperature effects (Figure 3c) are similar to, but larger than, those observed in range B (Figure 3b). The intensities of the octahedral bands increase slightly with temperature but a larger increase in the region 14–19 kK indicates tetrahedral nickel(II) species.[8] However, no discrete shoulders due to tetrahedral bands can be detected yet. Isosbestic points observed in these spectra have now shifted to lower energies.

Range D. The temperature effects here are dominated by the changes in absorption of two distinct nickel species, an octahedral and a tetrahedral complex.

At the lower end of the composition range, changes similar to those described for range C are observed (Figure 4), but partially resolved tetrahedral bands can now be distinguished with temperature increase. At higher chloride concentrations these bands become clearly resolved (Figure 5) and predominate above 20 mol % chloride (Figure 3d). At this point the octahedral band is reduced to a shoulder at about 19.20 kK. Isosbestic points are observed between the principal octahedral and tetrahedral transitions. The effect of temperature on the spectra of binary and ternary melts containing approximately the same mole per cent of chloride is compared in Figure 5 and will be discussed later.

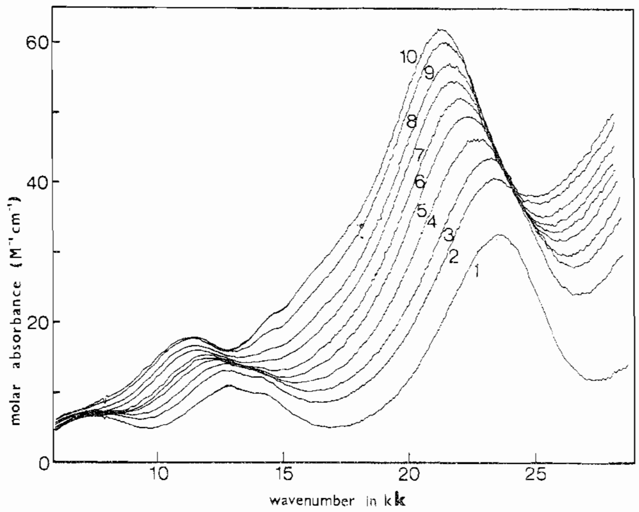

Figure 6. Effect of added chloride on spectrum of nickel(II) in a ternary melt at 214°. Chloride:nickel(II) mole ratios are respectively (1) 0, (2) 1.55, (3) 3.31, (4) 7.89, (5) 13.0, (6) 18.3, (7) 26.0, (8) 33.4, (9) 45.1, (10) 60.9.

Range E. The spectra of solutions in this composition range were relatively insensitive to changes in temperature. Small increases in the intensity of the tetrahedral bands were observed and the principal octahedral band was reduced to a weak shoulder at around 19.5 kK (Figure 3e). The spectra recorded in the pure chloride ternary melt (Figure 3f) did not change with time.

The Effect of Composition Changes on Spectra at Constant Temperature. To complement the series of temperature effects just described, an attempt was made to measure the effect, on the spectrum of nickel(II), of increasing the chloride composition of a nitrate melt at constant temperature. The spectra of two such runs were measured at 214 and 268°, using the ternary nitrate eutectic. In each case the chloride concentration was increased to (apparent) saturation (about 1.5 and 1.9 *M*, respectively). When the spectra at 214° (Figure 6) are compared with those recorded at approximately this temperature in constant composition runs, certain differences become apparent. A progressive shift to lower energy and an increase in the intensity of the principal octahedral band is observed as the chloride concentration is increased. Changes in the gradient of the spectra in the 14–19-kK region indicate the presence of small amounts of a tetrahedral nickel species at chloride compositions greater than 4 mol % (214°) and 3 mol % (268°). The octahedral band at around 12.5 kK is not significantly split into two components at compositions above 1 mol % chloride. The apparent isosbestic point will be discussed later.

Another approach gave further information. Data from the constant-composition studies were extrapolated to 300°. Typical results are summarized in Figures 7 and 8.

Internal Linearity Analysis of Nickel(II) Spectra in Mixed Nitrate–Chloride Melts. An internal linearity analysis was carried out at each composition where spectra generated an isosbestic point over a reasonable temperature range. The results of these computations are shown in Table IV for both binary and ternary melts.

All the sets of spectra at each composition studied (in Table IV) are internally linear. The important figures to compare are the rms (root-mean-square) deviations from the internal linearity constant β, calculated over the range 12.5–30.0 kK, and the deviation of the internal linearity function Δ. The internal linearity constant β is an averaged value over the

Table IV. Internal Linearity Analyses of Nickel(II) Spectra in Binary and Ternary Melts

Melt compn[a]			Temp of spectra, °C			Internal linearity const, β	Rms dev from			Shown in Fig.
Range	Mol % Cl^-		ϵ_1	ϵ_2	ϵ_3		β	% β	$\Delta, M^{-1}\ cm^{-1}$	
A	0.956	T	197	267	219	−1.030	0.274	27	0.98	3a
			233	267	219	0.463	0.029	6.3	0.11	
			291	267	219	1.373	0.234	17	0.47	
B	1.16	B	295	319	271	0.521			0.23	3b
			319	295	271	1.849			0.43	
C	3.93	T	243	256	220	0.549	0.086	16	0.36	3c
			289	256	220	1.462	0.108	7.4	0.43	
	3.99	B	269	320	245	0.304			0.27	...
			296	320	245	0.614			0.26	
D	7.05	T	239	272	248	−0.649	0.114	18	0.39	...
			260	272	248	0.607	0.085	14	0.17	
			284	272	248	1.460	0.125	8.5	0.30	
	7.55	B	284	330	259	0.352			0.26	4
			307	330	259	0.714			0.27	
	10.49	B	339	384	315	0.280			0.40	...
			361	384	315	0.608			0.44	
			339	361	315	0.548			0.17	
	17.25	T	283	295	272	0.548	0.066	12	0.18	5a
	18.46	B	377	400	355	0.519			0.26	5b
			400	377	355	2.027			0.54	
E	24.26	T	314	336	302	0.334	0.023	7	0.002[b]	3d
			325	336	302	0.683	0.035	5.2	0.002[b]	
			347	336	302	1.348	0.050	3.7	0.004[b]	
	28.12	T	344	366	333	0.380	0.075	20	0.21	...
			355	366	333	0.645	0.071	11	0.18	
			377	366	333	1.392	0.130	9.3	0.004[b]	

[a] B = binary melt; T = ternary melt. [b] Units of absorbance.

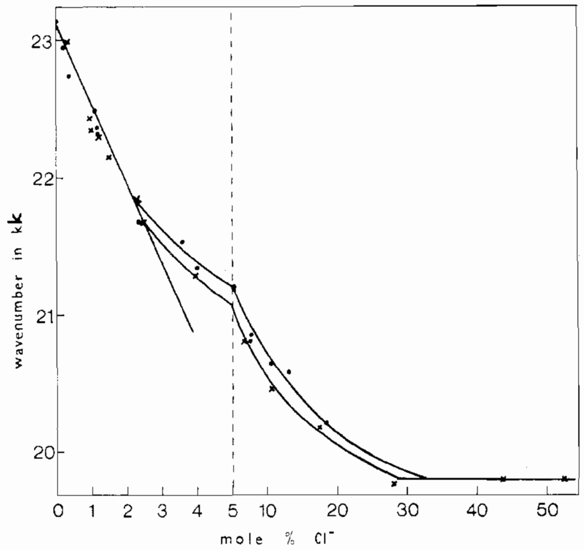

Figure 7. Variation in the energy of the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition of octahedral nickel(II) at 300° with the composition of mixed chloride–nitrate melts: ×, binary melts; ●, ternary melts.

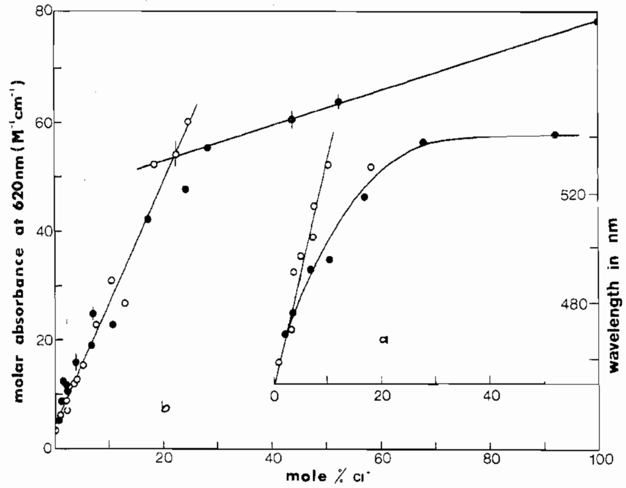

Figure 8. (a) Variation of the wavelength of the isosbestic point observed between the principal octahedral and tetrahedral transitions of nickel(II) as a function of melt composition: ○, binary melts; ●, ternary melts. (b) Change of absorbance at 300° of the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition of tetrahedral nickel(II) at 620 nm as a function of added chloride: ○, binary melts; ● ternary melts.

aforementioned range. Previously,[8] in calculating average β values, obviously unrealistic values were deleted before averaging. This is clearly unsatisfactory and a more rigorous approach is here employed which eliminates the need for making a judgement on each β_λ value in turn.

β_λ is computed at each digitized wavelength from

$$\beta_\lambda = (\epsilon_3 - \epsilon_1)/(\epsilon_2 - \epsilon_1) \qquad (1)$$

ϵ_1 and ϵ_2 being the reference spectra and ϵ_3 the sample spectrum. If ϵ_1 and ϵ_2 have very similar values, β_λ can be very large or can even change sign if instrumental noise makes ϵ_1 and ϵ_2 fortuitously cross at some wavelengths. A gate was therefore introduced: if the difference between spectra at any wavelength is less than a *threshold* value (set here at 0.01 absorbance unit), the corresponding value of β_λ is considered insufficiently accurate to warrant further averaging, and it is rejected. Other β_λ values are rejected if they lie outside a provisional value, β_P ± rms of β_P, determined from the remaining data points. From the acceptable data the reported mean β is determined, together with its rms deviation. The rms deviation of the internal linearity function Δ calculated from

$$\Delta_\lambda = (1 - \beta)\epsilon_1 + \beta\epsilon_2 - \epsilon_3 \qquad (2)$$

was obtained from Δ_λ values computed over *all* digitized wavelengths, whether or not they were rejected by the gate or in the averaging process. The computed Δ function, illustrated in Figure 4, is *not* offset from a mean value of zero, and thus a representative β is calculated by the averaging process. If an incorrect value of β is obtained, Δ will be displaced from zero and will change markedly in value on traversing the wavelengths of the isosbestic points.

The spectra of the acid and base forms of an indicator as a function of pH change have been studied and the internal linearity constants calculated.[20] Root-mean-square deviations of around 3% were obtained. However, since temperature changes affect spectra to some extent, the precision of the internal linear analyses obtained here will be reduced. Other errors may arise from the, at times, manual digitization of spectra at relatively large wavelength intervals. The rms deviation of β averages 10% and that of Δ rarely exceeds 0.5 M^{-1} cm^{-1} for all the compositions studied in Table IV. These values are comparable with those obtained for another temperature-sensitive equilibrium[21] and thus these spectra are acceptably internally linear with respect to temperature changes.

Generation of Spectra. Consider a set of spectra describing a two-species equilibrium. If experimental spectra (ϵ_1 and ϵ_2) are chosen as the two reference spectra, then a third spectrum (ϵ_3) may always be computed from any empirical value of β. This generated spectrum will always belong to the set of spectra internally linear with the reference spectra. If β is changed by small amounts and the resulting spectra are plotted and examined, a situation will be reached when the absorption due to one of the species is eliminated from the generated spectrum. A value of β is thus obtained which will generate the "terminal" spectrum of one component of the system relative to the reference spectra.

Smith and coworkers[8,11] have used this procedure at constant temperature, on varying the composition, to yield the spectra of various octahedral and tetrahedral nickel(II)–chloro species, but the spectra presented were manually smoothed. Terminal spectra obtained from temperature sensitive equilibria will contain more noise than those obtained from isothermal systems. While there are many mathematical procedures for smoothing data, such procedures were not employed here, in order to avoid the possible introduction of effects which might lead to erroneous results and conclusions. The appropriate β value that generated the terminal spectrum of one of the two species in equilibrium was the one that generated a spectrum having a base line absorbance of 3–5 M^{-1} cm^{-1} in the region of the other absorbing species.

Relationship between β and the Equilibrium Quotient. The term equilibrium quotient, rather than constant, will be used in this paper since neither the activities of the reacting species nor their temperature dependence is known.

Consider an equilibrium between two species in solution, $X \rightleftharpoons Y$, where (i) X and Y are the only absorbing species in the wavelength region studied, (ii) the total concentration, $c(T) = c(X) + c(Y)$, is constant, and (iii) the equilibrium is sensitive to temperature changes but the spectra of the individual species are invariant with respect to temperature. If $c(X)_1$ and $c(Y)_1$ are the concentrations of X and Y at temperature 1, etc., $\epsilon(X)$ and $\epsilon(Y)$ are the molar absorptions of the individual species X and Y at the wavelength under consideration, and ϵ_1 is the formal absorbance of the equilibrium system at temperature 1, etc., then assuming the law of additive absorptions and unit path length

$$\epsilon_1 = \epsilon(X)c(X)_1 + \epsilon(Y)c(Y)_1$$

This may be rewritten as

$$\epsilon_1 = (\epsilon(X) - \epsilon(Y))c(X)_1 + \epsilon(Y)c(T)$$

and similar expressions are obtained for ϵ_2 and ϵ_3, which may then be substituted into eq 1 to yield

$$(\epsilon_3 - \epsilon_1)/(\epsilon_2 - \epsilon_1) = (c(X)_3 - c(X)_1)/(c(X)_2 - c(X)_1) = \beta \qquad (3)$$

This relationship is made quantitative on introducing the β values which generate the terminal spectra of the component species X and Y.

If $\beta(X)$ and $\beta(Y)$ are the values associated with the individual spectra of X and Y, relative to the reference spectra recorded at temperatures 1 and 2 (such that $\beta(X) = (\epsilon(X) - \epsilon_1)/(\epsilon_2 - \epsilon_1)$), then when $\beta = \beta(X)$, $c(X)_3 = c(T)$, since the spectrum of X results from the conversion of all the absorbing species to X. Similarly, when $\beta = \beta(Y)$, $c(X)_3 = 0$ as there is no contribution from the spectrum of X to the generated spectrum of species Y. Hence eq 3 becomes

$$c(X)_3/c(T) = (\beta - \beta(Y))/(\beta(X) - \beta(Y)) \qquad (4)$$

This equation defines the linear relationship between the fractional concentration of one component of a two-species equilibrium ($c(X)_3/c(T)$) and the internal linearity constants β, $\beta(X)$, and $\beta(Y)$, all calculated relative to the same reference spectra. Knowing the total concentration of X and Y in the system, $c(T)$, the concentration of X and Y individually in solution at each temperature may be found from eq 4, that is, using a (correctly averaged) β value obtained, relative to the reference spectra, for each spectrum in the internally linear set. Hence an equilibrium quotient, K, can be defined and evaluated at each temperature studied. The enthalpy of the reaction, ΔH, is then obtained from the van't Hoff isochore $d(\ln K)/d(1/T) = -\Delta H/R$.

ΔH from Internal Linearity Theory. Some comments concerning the advantages and limitations of this new method for determining ΔH values must be made.

(i) The most valuable advantage of this method is that it does *not* depend upon the existence of a wavelength region in the set of spectra where only one species absorbs radiation, the requirement of previous procedures.

(ii) The derivation of the method involves the linear averaging and the linear extrapolation of data. No iterative least-squares procedures are used and equilibrium quotients are determined from simple expressions. Further, the method is efficient, one equilibrium quotient being calculated for each internally linear spectrum in a set greater than 3.

(iii) It is not necessary to record experimentally the spectra of the component species participating in the equilibrium. These are calculated in the course of the determination; however, criteria must be established whereby the terminal spectra can be recognized.

(iv) The method is limited by the constraints of the model equilibrium, the most important of which are the following.

(a) Only two light-absorbing species must be in solution, or if others are present, they must not absorb in the spectral region studied. This is a major limitation for stepwise reactions. If more than two species contribute to the measured absorption, the mathematical derivation cannot be simplified to eq 3. If three species absorb, and there is a simple relationship between two of them, then eq 3 can sometimes be obtained, and the system is treated as a pseudo-two-species equilibrium.[20]

(b) The spectra of individual species must remain invariant over the temperature range studied. There are many reports of the broadening, and also at times shifting, of the spectrum of a single species as the temperature is increased. In practice, this limitation means that the change in absorbance of an individual species must be small compared with the change arising from any shift in the equilibrium. This is the case for the present system.

(c) Ultimately, thermodynamic data are determined from the van't Hoff isochore, but this expression is only exact at a given temperature, and ΔH varies slightly with temperature. However, it is expected that the ΔH plots of the melts studied here will be linear over the temperature ranges employed.

Clearly, significant restrictions are placed upon the calculation of thermodynamic data from internal linearity theory, but the other spectroscopic methods currently available involve similar restrictions.

Calculation of ΔH for the Octahedral–Tetrahedral Equilibria. Equilibrium quotients and enthalpy values for the

Table V. Enthalpy Values by the Method of Internal Linearity for Nickel(II) Solutions in Binary and Ternary Melts

Melt compn[a]			Temp (ref spectra), °C				Generated octahedral band parameters			
Range	Mol % Cl^-				β_{oct}	β_{tet}	ν, kK	$\epsilon, M^{-1}\ cm^{-1}$	K_R' (extrapolated to 300°)	ΔH, kJ mol^{-1}
C	3.99	B	320	245	−3.0	17.5	21.4	56	0.22 ± 0.02	10.0 ± 1
D	7.05	T	272	248	−7.1	23.0	21.3	58	0.45 ± 0.02	18.0 ± 2
D	7.55	B	330	259	−3.5	9.8	21.4	61	0.48 ± 0.05	13.3 ± 2
D	10.49	B	361	315	−11.0	20.0	21.1		0.59 ± 0.05	8.4 ± 1
D	17.25	T	295	272	−12.0	14.5	20.9	80	0.99 ± 0.01	14.7 ± 2
D	18.46	B	400	355	−16.0	10.5	~20.5	80	1.2 ± 0.1	12.5 ± 2
E	24.26	T	336	302	−8.6	6.0	~21.0	85	1.4 ± 0.1	25.6 ± 2
E	28.12	T	366	333	−30.0	10.0	~20.4	84	2.5 ± 0.1	14.0 ± 2

[a] B = binary; T = ternary.

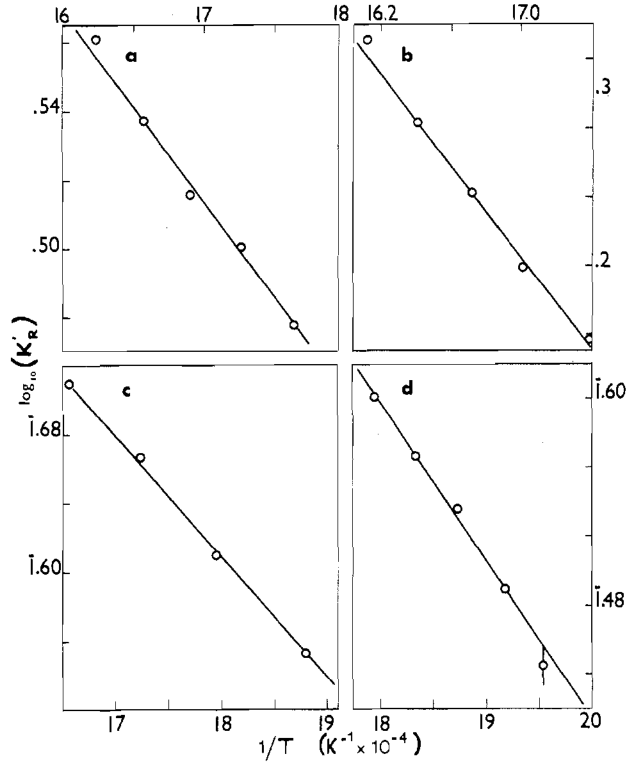

Figure 9. Examples of the linear plots obtained in determining ΔH by the method of internal linearity from the spectra of various solutions of $NiCl_2$ in alkali nitrate + chloride melts: (a) ternary melt + 28.14 mol % Cl^-; (b) ternary melt + 24.26 mol % Cl^-; (c) binary melt + 7.55 mol % Cl^-; (d) ternary melt + 7.05 mol % Cl^-.

temperature-dependent spectra recorded in the composition range 3.99–28.1 mol % chloride, in the binary and ternary melts, were calculated by the method of internal linearity and are summarized in Table V. The nature of the various equilibria occurring will be established in the following sections, and since all the equilibria involved octahedral to tetrahedral conversions, a generalized equilibrium quotient is defined at this stage as

$$K_R' = [\text{tetrahedral}]/[\text{octahedral}]$$

The results of a sample determination, that for the ternary system containing 24.26 mol % chloride, are given in Table VI. A selection of Arrhenius plots, from which ΔH was obtained, are presented in Figure 9. The values of K_R' were extrapolated to 300° from the enthalpy plots so that composition effects on K_R' could be compared (Table V).

The values of β_{oct} and β_{tet} in Table V refer to those β values which generate the individual octahedral and tetrahedral spectra of the species involved in the various equilibria. The two reference spectra yielding these values were chosen from the set recorded at each composition studied and from as wide a temperature range as was consistent with no decomposition.

Table VI. Equilibrium Quotients Calculated by the Method of Internal Linearity from the Spectra of Nickel(II) Solutions in a Ternary Melt Containing 24.26 Mol % Chloride

		Fraction[b] of species		
Temp, °C	β_T	Octahedral	Tetrahedral	K_R' [c]
302[a]	0.0	0.411	0.589	1.433
314	0.334	0.388	0.612	1.577
	0.344	0.387	0.613	1.581
325	0.683	0.364	0.636	1.746
	0.686	0.364	0.636	1.747
336[a]	1.0	0.343	0.657	1.920
347	1.348	0.319	0.681	2.138
	1.376	0.317	0.683	2.157

[a] Reference spectra. [b] $\beta_{oct} = -8.6$, $\beta_{tet} = 6.0$, fraction octahedral = $(\beta_T - 6.0)/14.6$. [c] K_R' extrapolated to 300°: 1.4 ± 0.1. ΔH determined graphically as 25.6 ± 2 kJ mol^{-1}.

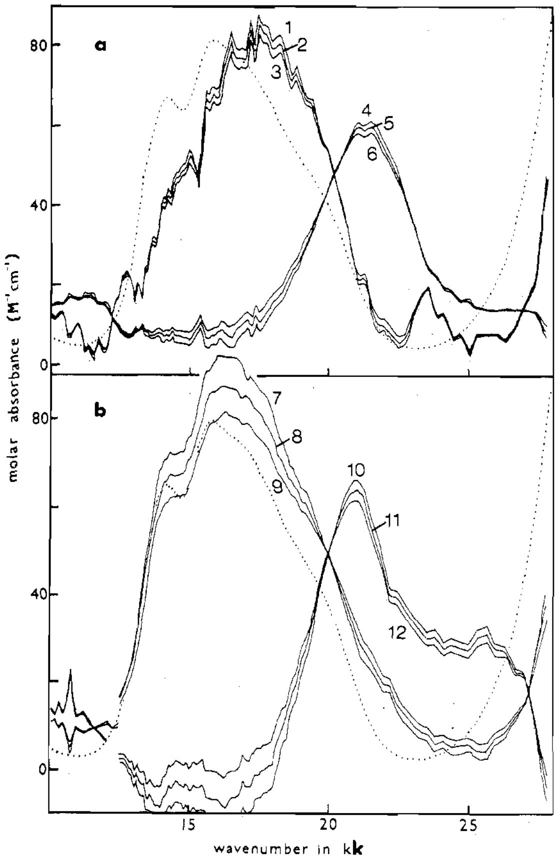

Figure 10. Generation of terminal spectra: (a) ternary melt + 7.05 mol % Cl^- + $NiCl_2$ (0.075 M); spectra generated from reference spectra recorded at 248 and 272°; (b) ternary melt + 24.26 mol % Cl^- + $NiCl_2$ (0.064 M); spectra generated from reference spectra recorded at 302 and 336°. Dotted curves represent the spectrum of $NiCl_4^{2-}$ in ternary chloride melt at 553°. β values: β_{tet}, (1) 24.0, (2) 23.0, (3) 22.0; β_{oct}, (4) −6.1, (5) −7.1, (6) −8.1; β_{tet}, (7) 7.0, (8) 6.0, (9) 5.0; β_{oct}, (10) −7.6, (11) −8.6, (12) −9.6.

Examples of generated spectra are given in Figure 10a and b.

Discussion

The presence of chloro complexes of nickel(II) in various nitrate eutectics containing small amounts of added chloride has been deduced from different electrochemical studies, the mono to the hexachloro complexes, inclusive, but excepting the penta species, being variously proposed.[22-26] From the present spectrophotometric studies it is possible to identify the presence of certain chloro- and chloronitratonickel(II) complexes in various mole per cent chloride ranges and between certain temperatures. The effects observed in the binary and ternary melts will be considered together, and the several differences discussed as appropriate. The solutions of nickel(II) in the pure nitrate and pure chloride melts are examined first.

Nickel(II) Solutions in Nitrate Melts and Chloride Melts. The spectra of nickel(II) dissolved in both binary and ternary nitrate melts are similar and result from an octahedral nitratonickel(II) complex. The coordination of nitrate ligands about a nickel ion gives an octahedral field, now attributed to the species $Ni(NO_3)_3^-$, in the ternary melt, nitrate behaving as a bidentate ligand in a distorted octahedral structure.[7]

The spectrum of nickel chloride dissolved in the ternary chloride mixture at 553° is related to that discussed by Brynestad, *et al.*,[8] in their extensive study of the binary melt system lithium chloride–potassium chloride. They showed that nickel was distributed between two types of centers, one basically octahedral and the other basically tetrahedral, which are in equilibrium. They initiated the description "center" since at their highest temperatures, around 1000°, the lifetime of a chloride contiguous to nickel would be considerably reduced. At lower temperatures, below 900°, they noted that spectral changes were quantitatively very regular and that the spectra behaved in a manner that paralleled the spectra of complex ions at ordinary temperatures in familiar solvents. Thus here, when the distribution of coordination geometries was tightly enclaved around an average, the product was a complex-ion-like entity. In this study, with temperatures generally below 400°, only complexes are observed.

Brynestad, *et al.*,[8] also concluded that, at low temperatures, the outer shells of tetrahedral centers were mostly potassium ions, and lithium ions surrounded the octahedral centers. Studies of nickel complexes in solution at ambient temperatures rarely consider the solvent molecules next to the ligands, but here there is some evidence concerning the identity of the neighboring cations, with sodium playing an intermediate role.[27]

It has long been contended that discrete complex ions do not occur in molten salts. Here we find positive evidence for their existence. Addition of very small amounts of chloride to nickel-containing nitrate melts produces large changes in the spectra, even at chlorine:nickel(II) mole ratios of less than 2, indicating that the chloride ions immediately become contiguous to nickel(II) ions. Studies in certain nonaqueous solvents have shown that when the halide:nickel(II) ratio just exceeds 4, the spectrum of the tetrahedral species is obtained, and this does *not* increase in intensity on further halide addition.[2,3] More important, the spectra of these complexes, and in particular their molar absorbances, are essentially identical in nonaqueous solvents and molten salts.

Identification of Complexes in Range A. In both the binary and ternary melts only octahedral complexes were identified in this range.

On addition of small concentrations of chloride ions, a large initial shift in the octahedral $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition (Figure 7) is observed, and a linear dependence occurs between the energy of this transition and the melt composition. Angell and Gruen[28] have noted that this transition shifts linearly about −1.4 kK for every two chloride ions substituted into hydrated nickel(II) octahedra. In Figure 7 such a shift occurs in this composition range.

The reduction in symmetry of a complex produces an increase in the intensity of the associated absorption bands and hence there is a regular substitution of chloride ions into nickel octahedra with increasing chloride concentration. Three species are present in solution in significant concentrations: $Ni(NO_3)_3^-$ and the mono- and dichloronitratonickel complexes.

The monochloro species will be $NiCl(NO_3)_3^{2-}$, with two bidentate and one monodentate nitrate ligands; the dichloro species can be either $NiCl_2(NO_3)_3^{3-}$, with one bidentate and two monodentate nitrates, or $NiCl_2(NO_3)_2^{2-}$, with both nitrates bidentate. The dichloro species probably has trans geometry.

The splitting of the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition is evidence for the complex $Ni(NO_3)_3^-$ since this transition readily splits in symmetrical octahedral fields.[29] As the splitting disappears above 1.2 mol % chloride, above this concentration this complex is lost. The requirement of a symmetrical octahedral field to split this band suggests that the next shell contains identical cations, thus sodium ions only in the binary melt and lithium only in the ternary melt. The presence of these three nickel species explains why no isosbestic points nor accurate internal linearity analyses were obtained for spectra in this composition range.

The System Obtaining in Range B. Spectra of solutions in this composition range have a *small* temperature dependence (Figure 3b), generate isosbestic points and show acceptable internal linearity (Table IV). Such phenomena could be caused by the effect of temperature on the spectrum of a single octahedral species.[30] Isosbestic points would then result from a combination of a shift in the energy of a transition caused by temperature induced perturbations in the vibronic mechanism of excitation[31] and a reduction in intensity due to the thermal broadening of the band.[30]

However, noting the continuing shift in the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition energy (Figure 7), we conclude that these changes represent a temperature-dependent equilibrium between two octahedral chloronickel species, *viz.*

$$NiCl(NO_3)_3^{2-} + Cl^- \rightleftharpoons NiCl_2(NO_3)_x^{x-}$$

where x is 2 or 3 (*vide supra*). An increase in temperature or chloride concentration shifts this equilibrium in favor of the dichloro species. The observed temperature dependence and unique isosbestic points (Figure 3b) arise from small shifts in the relative intensities of two overlapping bands separated by perhaps 0.7 kK.[28]

Gruen and McBeth,[5] using lithium nitrate–potassium nitrate eutectic, also obtained an isosbestic point at around 23 kK (their Figure 4) but did not remark on it. Since this point did not appear at a chlorine:nickel(II) ratio of 1.55, but at 3.31, all the chloride added initially formed the monochloro complex and the isosbestic point relates to the monochloro–dichloro equilibrium. However their molar absorbance values were about half ours for the ternary melt. This suggests less symmetry about the nickel complexes in our system. In their binary system the cations surrounding the complexes will be mainly lithium ions; in the ternary system sodium will compete with potassium for the remaining available places, causing an additional loss of symmetry and hence an increase in the number of vibrationally allowed transitions.

The Intermediate Nature of the System in Range C. The temperature dependence of spectra in this composition range resembles that in range B, except that the increase in absorbance in the 14–19-kK region is larger than that expected for the thermal broadening of a single band or that expected from small shifts in an octahedral–octahedral equilibrium.

Tetrahedral nickel complexes are formed, since above 3 mol % chloride the shift of the octahedral transition maximum decreases with added chloride (Figure 7), and the absorbance at 16 kK, near the maximum of the $NiCl_4^{2-}$ species, swells in intensity. The changes in spectra may be rationalized in terms of an octahedral–tetrahedral equilibrium, between the dichloronickel species and a tetrahedral species (which will later be identified). The concentration of this species is small and the complex band structure of the tetrahedral $^3T_1(F) \rightarrow {}^3T_1(P)$ transition cannot be resolved from changes between spectra in the 14–19-kK region. Thus this composition range is viewed as an extension of range D.

Species and Reactions Occurring in Range D. Spectral changes in this range are dominated by shifts in an octahedral–tetrahedral equilibrium. An increase in both temperature and chloride concentration shifts the equilibrium in favor of the tetrahedral species.

(a) Tetrahedral Species. The ambient spectra of the tetrahedral species $NiCl_3S^-$, where S is a nonaqueous solvent, have been recorded,[4,32-35] and all display two peaks close to 14.2 and 16.1 kK and have a pronounced shoulder around 17.2 kK. The energy levels in these complexes are thus determined largely by the chloride ligands, the various weakly bonded solvent molecules having little effect. The peak maxima for nickel(II) in chloride melts containing lithium ions are close to these values. The solvated complexes have essentially C_{3v} symmetry, but the distorted $NiCl_4^{2-}$ species in molten chlorides has previously been described as tetragonally distorted,[36] toward D_{2d} symmetry. It is now here proposed that the distortion from regular symmetry obtaining in lithium-containing melts is toward C_{3v} symmetry, with one lithium cation interacting specifically with one of the four chloride ligands. This complements the conclusion of Brynestad, *et al.*,[8] that in lithium chloride–potassium chloride melts $NiCl_4^{2-}$ is largely surrounded by potassium ions and that on increasing the temperature the spectrum tends to that of a less distorted $NiCl_4^{2-}$ species, such as is found in alkali halide melts where lithium ions are absent;[27,37] the lithium ion is thus replaced by potassium at high temperatures.

The tetrahedral complex here may thus be either $NiCl_3(NO_3)^{2-}$ or $NiCl_4^{2-}$, both having essentially C_{3v} symmetry. In this composition range the former species is present because in Figure 8b the absorbance at 16 kK, corrected for temperature, is linear up to 24 mol % chloride and then follows another linear relationship above this composition up to 100 mol % chloride. The binary melt, which does not contain lithium ions, does not change slope at all, and the ternary melt does not change slope abruptly. This plot closely resembles mole ratio plots where a change in slope represents a change in the identity of the species reacting. The variation in the wavelength of the isosbestic point observed between the principal octahedral and tetrahedral absorption bands (Figure 8a) also indicates that the shell around $NiCl_3(NO_3)^{2-}$ contains significantly different cations in the binary compared with the ternary melt system. Gruen and McBeth[5] have intimated the presence of $NiCl_4^{2-}$ in their eutectic when saturated with added chloride: we would now conclude that they had formed $NiCl_3(NO_3)^{2-}$.

(b) Octahedral Species. The absorption maximum of the octahedral nickel species shifts from an observed value of about 22.2 kK at 3 mol % chloride to a limiting value of around 19.8 kK at around 22 mol % chloride (Figure 7). At these higher concentrations, this octahedral transition is reduced to a weakly resolved absorption which is extensively overlapped by the dominant tetrahedral bands (Figure 3d). This shift means that the same octahedral species cannot be present throughout the current composition range, and the variation in the wavelengths of the isosbestic points supports this (but see later).

The lowest octahedral transition readily identifies the hexachloro octahedral species, especially in the lithium-containing melts.[8] Thus in this composition range the octahedral complex changes from $NiCl_2(NO_3)_x^{x-}$ to $NiCl_6$ (the charge is here omitted since this species has not been identified in nonaqueous solvents and may therefore be considered as a center).

(c) Generated Spectra. The terminal spectra, of the octahedral and tetrahedral species participating in the equilibria in this concentration range, were generated. Typical results are shown in Figure 10a, which illustrates extrapolated spectra obtained at the lower end of the concentration range. Figure 10b contains spectra produced from the beginning of range E. Both figures contain the spectrum for nickel chloride in a ternary chloride melt, and only in the latter figure is the profile of $NiCl_4^{2-}$ resembled by the generated spectra. In Figure 10a this transition is at 21.3 kK, in the direction of nitrato species. The marked difference between the profile of $NiCl_4^{2-}$ and that of the tetrahedral species in solution reinforces our above proposal that here the species is $NiCl_3(NO_3)^{2-}$.

The octahedral bands, now clearly resolved at around 21.3 and 20.8 kK in Figure 10a and b, respectively, merit greater confidence. The latter transition, in 24.24 mol % chloride, is close to that for the octahedral hexachloronickel species obtained in nickel-doped chlorides.[28,38] Employing the rule of average environment[39] the ratio of chloride to nitrate for the 21.3-kK transition is very close to 5.

Thus in this concentration range the equilibrium is initially largely

$$NiCl_5(NO_3) \rightleftharpoons NiCl_3(NO_3)^{2-} + 2Cl^-$$

As the concentration of chloride is increased, the equilibrium changes until, around 22 mol % chloride, it is essentially

$$NiCl_6 \rightleftharpoons NiCl_4^{2-} + 2Cl^-$$

The nature of the system in range C thus becomes clearer, the dichloro species is there rapidly converted to the pentachloro species as chloride is added in this narrow concentration range, and only when the latter species is present does further chloride addition, or temperature increase, bring about interconversion to the tetrahedral species. The rapid and linear shift of the octahedral transition with added chloride up to about 7 mol % chloride in Figure 7, followed by steady curvature up to around 25 mol % chloride, and then no further shift, augments this conclusion.

The System Obtaining in Range E. An increase in chloride concentration in this range causes the spectra of the nickel-containing solutions to resemble more and more those obtained in lithium chloride–potassium chloride melts.[8] Thus in line with the above discussion, we conclude that only one equilibrium is now present

$$NiCl_6 \rightleftharpoons NiCl_4^{2-} + 2Cl^-$$

The features of Figures 7 and 8 support this assignment, and if the isothermal equilibria (K_R' at 300° in Table V) are plotted against mole per cent chloride, the data are linear only up to 25 mol % chloride.

Enthalpy Values. The ΔH values reported in Table V are much less than those reported for octahedral–tetrahedral equilibria involving various chloronickel complexes in aqueous,[1] nonaqueous,[3,4,40] and fused-salt systems.[28,41] However, due to the nature of the present system the precision of these values is obviously less than for values calculated in other ways from spectrophotometric data, but certain trends can be here identified.

The average of the results for the binary system is 11 kJ mol^{-1}, and that for the ternary, excluding the two highest chloride concentrations, is 16.4 kJ mol^{-1}. When individual values at almost identical chloride concentrations are compared, the same difference is seen. Since the two equilibria present in this range are identical in that, as well as the octahedral–tetrahedral change, they both eject two chloride ions, then ΔH values would be expected to be the same within experimental error. The role of the lithium ion is thus evident.

The lowest enthalpy value so far recorded for octahedral–tetrahedral equilibria involving chloronickel complexes is found by Angell and Gruen[28] for $NiCl_6 \rightleftharpoons NiCl_4^{2-}$, and it was attributed to the energy of the configurational change. Other equilibria, typically involving the replacement of one or more solvent molecules by chloride, usually had ΔH values around 60 kJ mol^{-1}. The nitrate ions which surround each nickel species therefore contribute to a reduction in the potential energy difference between the octahedral and tetrahedral species; the lithium cations have an opposite effect. Thus in the equilibrium $NiCl_5(NO_3) \rightleftharpoons NiCl_3(NO_3)^-$ the nitrate ions, which are greater in abundance than chloride around each species, will, because of their disk shape, facilitate the removal of the exiting chloride ligands into the bulk melt. When lithium ions are present, they will, as previously argued, dominate the cation component of the shell around the octahedral species. Their large polarizing power will mitigate against the ready withdrawal of chloride ions into the melt structure. They probably migrate with the chloride ions, as lithium chloride ion pairs, so that their place is then taken by potassium ions, now around a tetrahedral species.[8]

Conclusions

When chloride ions are added to nitrate melts containing nickel(II), they immediately enter the first coordination sphere around the nickel. This argues for some form of covalent bonding between nickel and chloride and hence the formation of a *complex ion*. On applying the conventional techniques for establishing the presence and identity of complex ions (of nickel and other transition metals) in nonaqueous solvents at ambient temperatures the following mixed-ligand complex ions were identified with reasonable certainty in molten nitrates containing added chloride: $NiCl(NO_3)_3^{2-}$, $NiCl_2(NO_3)_3^{3-}$ (or possibly $NiCl_2(NO_3)_2^{2-}$), and $NiCl_3(NO_3)^{2-}$. The species $NiCl_5(NO_3)$ and $NiCl_6$ were found but not assigned a charge as they have not been reported in nonaqueous solvents and identified as octahedral complex ions.

The presence of lithium ions in the nitrate melts produces certain specific effects, which are also reflected in the enthalpy values obtained by a new technique for the various two-species equilibria that are observed at various concentrations of added chloride. The unusually low values obtained reflect properties of a melt system containing both disk-shaped and spherical ions.

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Registry No. $LiNO_3$, 7790-69-4; $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1; LiCl, 7447-41-8; NaCl, 7647-14-5; KCl, 7447-40-7; $NiCl_2$, 7718-54-9; $NiCl(NO_3)_3^{2-}$, 54120-21-7; $NiCl_2(NO_3)_3^{3-}$, 54120-22-8; $NiCl_2(NO_3)_2^{2-}$, 54120-23-9; $NiCl_3(NO_3)^{2-}$, 54120-19-3; $Ni(NO_3)_3^-$, 54120-20-6; $NiCl_4^{2-}$, 15320-56-6.

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