A New Computer-based Method for Determining ΔH from Digitized Spectra: the Nickel(II) + Chloride System in Dimethyl Sulphoxide

By **Trevor R. Griffiths** * and **Philip J. Potts**, Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

A new method is described for calculating equilibrium quotients and enthalpy values from digitized spectra, for two-species equilibria, based on the concept of internal linearity. The method is evaluated by comparing the results obtained with those reported earlier [1] for the system nickel(II) + chloride in dimethyl sulphoxide: the results agree well. Fourth-derivative curves of the digitized spectra are computed and permit definitive identification of the species present in solution at any one time, and hence the temperature range over which the two-species equilibrium $[NiCl_2(dmso)_4]^0 + Cl^- \rightleftharpoons [NiCl_3(dmso)]^-$ occurs can be precisely determined. The derivation of the relationship between ΔH and β, the internal linearity constant, and the computing principles employed, are given in the Appendix.

OUR earlier investigation [1] upon the influence of temperature and concentration upon chloride-nickel(II) interactions in dimethyl sulphoxide (dmso) identified, from the absorption spectra, the chloro-complexes formed and determined the enthalpy of the equilibrium reaction $[NiCl_2(dmso)_4]^0 + Cl^- \rightleftharpoons [NiCl_3(dmso)]^- +$ 3 dmso. Digitizing equipment has now been attached to our spectrophotometer, and commissioning tests have been completed. Several computer programmes have been developed which yield additional chemical information not readily accessible from experimental data. The tests consisted of a re-examination and extension of our earlier findings, especially since we had developed a new computer-based technique for determining enthalpy values from absorption spectra. We therefore needed to compare our results with those from a system with which we were already familiar. The technique is here described and the results agree within experimental error. Further valuable information is also generated. Since digitizing procedures and some essential details of computing programmes have not been described in the few papers which have discussed computer calculations on absorption spectra, our procedures are summarized in the Appendix.

EXPERIMENTAL

The details given earlier [1] were followed, except that a new furnace was used, based on a design by Boston and Smith,[2] in which our dmso solutions could be maintained to within ±0·2 °C. Spectra were here corrected for the thermal expansion of dmso.

The digitizing equipment consisted of a modification to the Applied Physics Cary 14H spectrophotometer to receive two shaft encoders, one attached to the pen mechanism and the other to the wavelength drive mechanism. These were connected to a decoder/trigger unit, all supplied by Harrison Instruments Ltd., Farnborough, Hants. The output was fed to a high speed paper-tape punch, model 4070, supplied by Facit-Odhner Electronics, Ltd. The system is illustrated diagrammatically in Figure 1. The interfacing and other technical details will be published elsewhere.

RESULTS

A selection of the spectra recorded of a solution in dmso of chloride + nickel(II), mole ratio 4·45, is shown in

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[1] T. R. Griffiths and R. K. Scarrow, *J. Chem. Soc.* (*A*), **1970**, 827.

[2] C. R. Boston and G. P. Smith, *J. Sci. Instr.*, **1969**, **2**, 543.

Figures 2 and 3. The spectra, automatically digitized at 2 nm intervals, were obtained by difference. The data points, plotted on a computer-driven graph-plotter, are connected by straight lines: the originally recorded charts consisted of much smoother curves. Although various smoothing procedures are available all our calculations were performed upon the raw data to avoid any artificial smoothing or unwarranted reduction in subsequently calculated standard deviations.

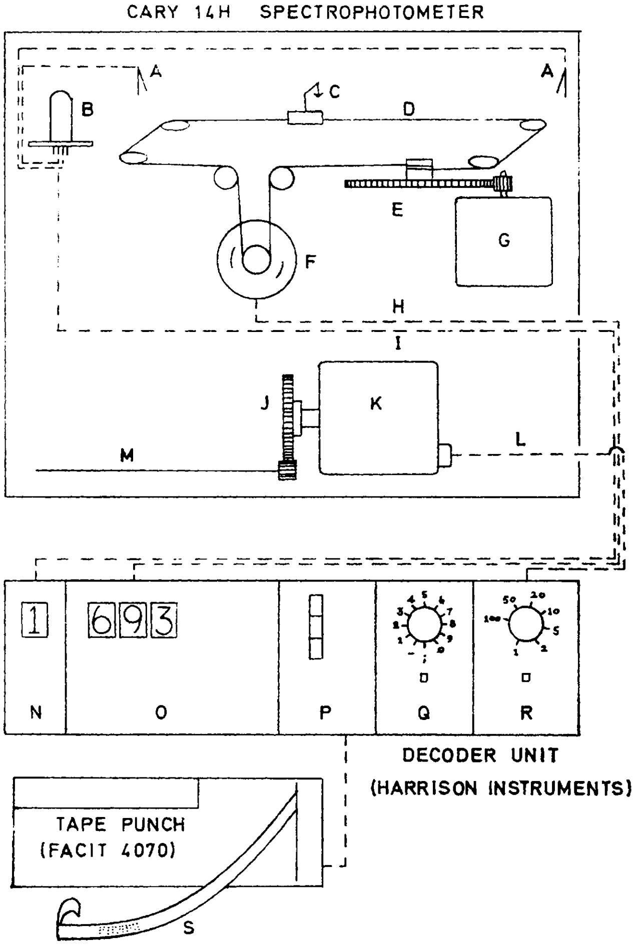

FIGURE 1 Diagrammatic representation of the digitizing system coupled to the Cary 14H spectrophotometer. A, microswitch; B, chart-scale relay unit; C, pen; D, pen-drive wire; E, pen-drive gears; F, absorbance encoder; G, pen-drive motor; H, digitized absorbance-signal path; I, digitized chart-scale absorbance-range signal-path; J, anti-blacklash gear; K, wavelength encoder; L, digitized wavelength-signal path; M, monochromator-drive shaft; N, scale-range decode unit; O, absorbance decoder; P, punch parity selector; Q, auxiliary code inject unit; R, digitizing interval selector; S, punched tape

The mole ratio of 4·45 was selected for study here after plotting the estimates given previously [1] of the fractions of $[NiCl_4]^{2-}$ and $[NiCl_3(dmso)]^-$ against mole ratio at various temperatures. At around 4·5 the maximum concentration of $[NiCl_4]^{2-}$ is less than 2% at 50 °C, and decreases further at higher temperatures. In Figures 2 and 3 the absorption maxima at 16·05 and 14·50 kK,* and the shoulder at around 16·95 kK, increase with increasing temperature: these bands are associated with the complex $[NiCl_3(dmso)]^-$. The tetrahedral complex $[NiCl_4]^{2-}$ is identified with absorption bands centred at 15·3 and 14·3 kK, and no bands in these positions were found at this mole ratio. Thus significant concentrations of only one tetrahedral species, $[NiCl_3(dmso)]^-$, are found in this system.

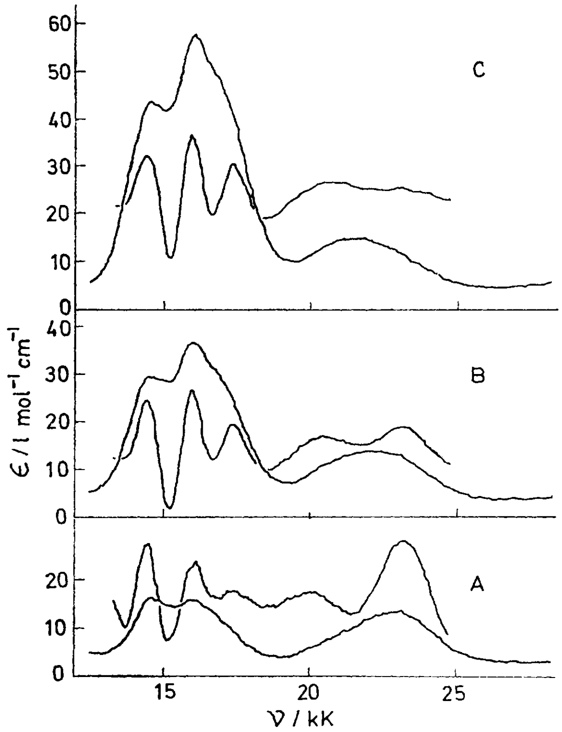

FIGURE 2 Absorption spectra and fourth-derivative functions of Ni^{II} + 4·45 Cl^- solutions in dmso recorded at A, 69·2 °C; B, 92·1 °C; and C, 111·4 °C. Derivative curves computed by the method of differences from the integer set 15, 14, 13, 11

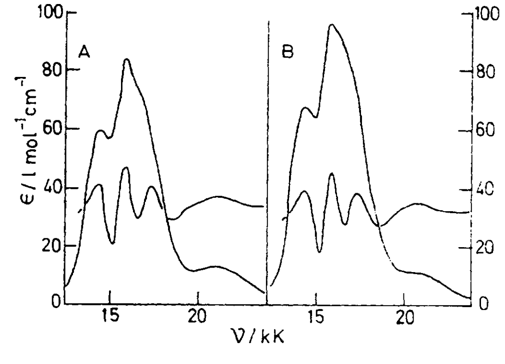

FIGURE 3 Absorption spectra and fourth-derivative functions of Ni^{II} + 4·45 Cl^- solutions in dmso recorded at A, 143·2 °C; and B, 174·9 °C. Derivative curves computed from the integer set 15, 14, 13, 11

* 1 kK = 10^3 cm^{-1}.

Three octahedral species have been reported in nickel(II) + added chloride in dmso.[1] These species had a single absorption maximum in the visible region, *viz.*,

$[Ni(dmso)_6]^{2+}$: 24·04 kK, ε = 10·15 l mol^{-1} cm^{-1} (ref. 3),
$[NiCl(dmso)_5]^{+}$: 23·1 kK,[1]
$[NiCl_2(dmso)_4]^0$: 21·2 kK.[1]

The octahedral peak maximum observed here shifts from 23·5 kK at 21·1 °C to 20·3 kK at 174·9 °C, when it is a weakly resolved shoulder on the edge of the intense tetrahedral bands. The octahedral species have bands which are too broad and close to appear as discrete peaks, but from the position of the observed maximum the species present, and their approximate proportions, can be determined. At ambient temperature the predominant species is $[NiCl(dmso)_5]^+$, in equilibrium with a small amount of $[Ni(dmso)_6]^{2+}$. Above 120 °C, all the octahedral nickel is in the form $[NiCl_2(dmso)_4]^0$.

Figure 4 shows the relative proportions of the nickel complexes present at this mole ratio as a function of temperature.

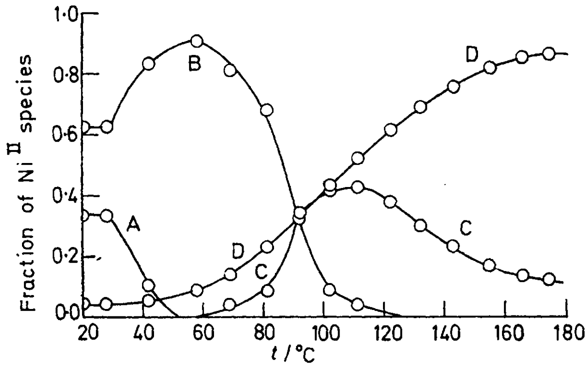

FIGURE 4 Variation in concentration of various nickel^{II} complexes in Ni^{II} + 4·45 Cl$^-$ solutions in dmso from 21 to 175 °C. A, $[Ni(dmso)_6]^{2+}$; B, $[NiCl(dmso)_5]^+$; C, $[NiCl_2(dmso)_4]^0$; D, $[NiCl_3(dmso)]^-$

Fourth Derivative Functions.—The fourth (and second) derivative curves of a spectrum, or similar profile, reach maximum (and minimum) values at energies corresponding to the maximum absorbance of component bands in the spectrum. Fourth-derivative curves show clearly all bands present including weak bands, or species present in very low concentrations, and such curves were computed for the spectra measured. Examples are given in the Figures 2 and 3.

The resolved absorption maxima are listed in Table 1. The derivative functions clearly resolve three maxima at 14·45, 15·95, and 17·4 kK, which may be identified with the tetrahedral species $[NiCl_3(dmso)]^-$. No bands arise at the absorption maxima of the $[NiCl_4]^{2-}$ species.

The weak octahedral bands are only resolved below 100 °C from the fourth-derivative curves, maxima arising at 20·85 and at 23·1 kK, and assigned to the species $[NiCl_2(dmso)_4]^0$ and $[NiCl(dmso)_5]^+$ respectively. Only the maximum of the former species is seen at temperatures above 111 °C.

Δ*H Determination by Conventional Analysis.*—The fraction of the tetrahedral species $[NiCl_3(dmso)]^-$ present in solution may be found by comparing the formal absorbance at 16·00 kK for the temperature-dependent spectra with the molar absorbance of this species. Unfortunately the spectrum of this complex, completely free from other nickel species, has not been reported. The molar absorbance value used previously [1] in the calculations for Δ*H* was not given, but was 128 l mol^{-1} cm^{-1}. The validity of this choice was therefore not then examined, and we now do so.

TABLE 1

Fourth-derivative maxima as a function of temperature

	Resolved absorption maxima (kK)				
t/°C	Tetrahedral $[NiCl_3(dmso)]^-$ bands			Octahedral bands	
69·2	14·46	16·16	17·40	20·06	23·20
92·1	14·45	15·98	17·34	(20·05) *	(23·09)
111·4	14·45	15·95	17·39	(20·87)	(22·88)
143·2	14·45	15·95	17·42	(20·88)	
174·9	14·45	15·97	17·37	(20·86)	

* Brackets indicate that the fourth-derivative maximum is weakly resolved. Derivative functions calculated by the method of differences from the integer set (15, 14, 13, 11)—see Appendix.

Since the molar absorbance values of the peak maxima for $[NiCl_3(solvent)]^-$ are not constant with solvent change [4-6] it was decided to recalculate Δ*H* using values at $\varepsilon_{16.00\,kK}$ of 100, 110, 120, 130, and 140 l mol^{-1} cm^{-1}. An equilibrium quotient * was defined by $K_2' = [NiCl_3(dmso)^-]/[NiCl_2(dmso)^0][Cl^-]$ and its variation with temperature determined by the method described previously,[1] and with improved accuracy as the new furnace had a smaller temperature gradient. The family of plots of $\log_{10}(K_2')$ against reciprocal temperature from $\varepsilon_{16.00\,kK}$ values of 100 to 140 l mol^{-1} cm^{-1} are compared in Figure 5a.

The gradients of these Δ*H* plots are relatively insensitive to the molar absorbance value chosen for $[NiCl_3(dmso)]^-$ below 110 °C but there is a two-species equilibrium at temperatures above 110 °C and here the Δ*H* plots obtained from values above 110 l mol^{-1} cm^{-1} curve from linearity in an opposite direction to the plot for the 100 l mol^{-1} cm^{-1} value. Extrapolation shows that $\varepsilon_{16.00\,kK}$ = 108 l mol^{-1} cm^{-1} gives a linear Δ*H* plot with a gradient equivalent to 53·9 kJ mol^{-1}. The curvature of the plots at low temperature is due mainly to the appearance of the monochloro octahedral complex. A similar effect was observed by Furuhashi *et al.*[7] in solutions of nickel chloride in *NN*-dimethylformamide.

Δ*H Determination by the Method of Internal Linearity.*—(a) *Calculation of the internal linearity constant* β_T. When a system at equilibrium is constrained to change its equilibrium position by the application of an external parameter, for example, temperature, composition, pH, pressure, *etc.*, and the total concentration of the two interacting species

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* The term quotient is here employed, rather than constant, as activity coefficients, and their temperature dependence, are not known.

[3] D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, 1962, **1**, 285.

[4] D. F. C. Morris and D. N. Slater, *J. Inorg. Nuclear Chem.*, 1965, **27**, 250.

[5] D. A. Fine, *Inorg. Chem.*, 1965, **4**, 345.

[6] C. P. Nash and M. S. Jenkins, *J. Phys. Chem.*, 1964, **68**, 356.

[7] A. Furuhashi, K. Fukumoto, S. Kawai, and Y. Hayakawa, *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, 1971, **39**, 569.

remains constant, only their relative concentrations varying, then the spectra recorded are commonly found to contain one or more isosbestic points at wavelengths where the two absorbing species have the same molar extinction coefficients. In this study an isosbestic point was observed at 19·6 kK for spectra recorded above 120 °C.

Such evidence is not necessarily diagnostic for a two-species equilibrium,[8] but the evidence given above suggests this concept for the present system. Brynestad and Smith [8] have proposed that the relationship between sets of spectra should be investigated over a range of wavelengths rather than from deductions based on the observation of an isosbestic point at one particular wavelength.

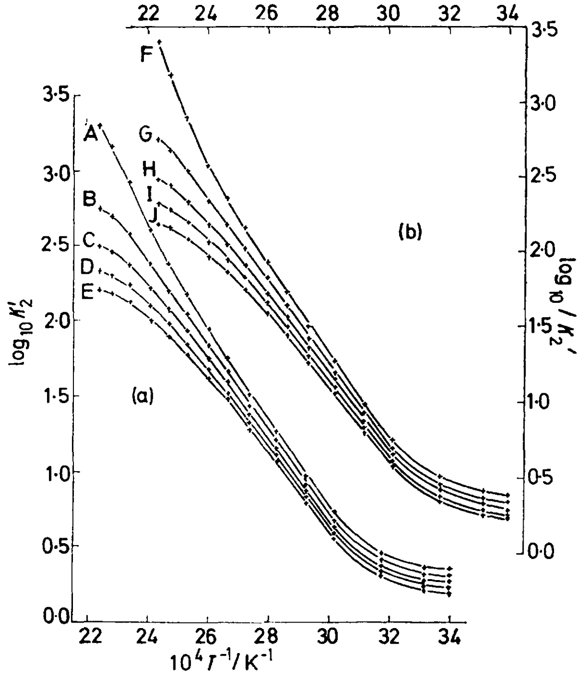

FIGURE 5 ΔH plots from the spectra of Ni^{II} + 4·45 Cl^- solutions in dmso. (a) Conventional analysis: curves calculated from assumed values for $\varepsilon_{16.00\ kK}$ of $[NiCl_3(dmso)]^-$ of A, 100; B, 110; C, 120; D, 130; and E, 140 l mol^{-1} cm^{-1}. (b) Internal linearity analysis relative to spectra at 132·1 and 166·0 °C. Values for $\varepsilon_{16.00\ kK}$ of $[NiCl_3(dmso)]^-$ assumed to be F, 100; G, 110; H, 120; I, 130; and J, 140 l mol^{-1} cm^{-1}

They showed that, under certain conditions, any one *spectrum* in a set may be generated by a linear combination of two other spectra, termed reference spectra, from that set. The symbol β was used to describe the internal linearity relationship between the three spectra. β Is a monotonous function [8] of the applied external parameter and is independent of wavelength. Hence, if any two spectra in an internally linear set intersect, then this crossing point must be an isosbestic point: conversely, the presence of an isosbestic point does not necessarily prove that the set is internally linear. This concept has been applied [9] to an equilibrium between chloronickel complexes in molten salts, at constant temperature, as a function of melt composition. We now apply it for the first time to a system in which temperature is the external parameter, and from which β_T is obtained, and subsequently enthalpy values. Details of procedures for computing spectra and obtaining acceptable values of β_T are given in the Appendix.

All spectra vary slightly as the temperature of the system is changed, a slight broadening commonly being observed. For the present system such changes are small over the limited temperature range studied. Had they been large the isosbestic point may not have been observed. An examination of related octahedral and tetrahedral complexes of nickel, and cobalt, revealed that below a 100 °C temperature range the spectra changed little in shape and position.[10-12] Any marked changes in spectra with temperature have been attributed to configurational changes of, or around, the complex.[9,13-16] Thus r.m.s. (root mean square) deviations of β_T can be expected to be slightly greater than those obtained for a two-species equilibrium where temperature is not the external parameter.[17] Additionally, we should find sets of internally linear spectra where one of the set passes close to, but not through, the observed isosbestic point.

The constant of internal linearity β_T was therefore computed for each of the spectra recorded over the range 21—175 °C. The results are given in Table 2. The spectra at 132·1 and 166·0 °C were chosen as reference spectra because they were reasonably well separated from each other and yet lay within the temperature range for which a two-species equilibrium had been established.

TABLE 2

Internal linearity analysis of the spectra of Cl/Ni = 4·45 in dmso as a function of temperature

t/°C	β_T [b]	R.m.s. deviation from β_T		R.m.s. deviation of Δ
			%β_T	l mol^{-1} cm^{-1}
21·1	−3·696	0·351	9·5	5·6
28·3	−3·654	0·329	9·0	5·6
42·1	−3·596	0·327	9·1	5·6
58·4	−3·398	0·301	8·9	5·1
69·2	−3·103	0·257	8·3	4·5
81·3	−2·595	0·214	8·2	3·6
92·1	−2·071	0·154	7·4	2·6
102·3	−1·499	0·105	7·0	1·7
111·4	−0·996	0·054	5·5	1·0
122·2	−0·429	0·024	5·7	0·4
132·1 [a]	0·0			
143·2	0·391	0·023	5·8	0·4
155·2	0·777	0·030	3·9	0·4
166·0 [a]	1·0			
174·9	1·100	0·037	3·4	0·5

[a] Reference spectra. [b] Calculated over the wavenumber range 12·5—20·0 kK. Threshold difference in absorbance: 0·01 absorbance units (≡1·1 l mol^{-1} cm^{-1}).

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[8] J. Brynestad and G. P. Smith, *J. Phys. Chem.*, 1968, **72**, 296.

[9] J. Brynestad, C. R. Boston, and G. P. Smith, *J. Chem. Phys.*, 1967, **47**, 3179.

[10] J. R. Dickinson and K. E. Johnson, *J. Mol. Spectroscopy*, 1970, **33**, 414.

[11] J. R. Dickinson, personal communication.

[12] D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, 1963, **6**, 23.

[13] O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, 1957, **26**, 1686.

[14] T. S. Mityaeva and I. S. Pominov, *Russ. J. Inorg. Chem.*, 1969, **14**, 1739.

[15] J. Brynestad, H. L. Yakel, and G. P. Smith, *J. Chem. Phys.*, 1966, **45**, 4652.

[16] G. P. Smith, C. R. Boston, and J. Brynestad, *J. Chem. Phys.*, 1966, **45**, 829.

[17] T. R. Griffiths and P. J. Potts, *Analyt. Chim. Acta*, 1974, **71**, 1.

Calculations were confined to the wavenumber range 12·5—20·0 kK, where differences between spectra were greatest.

Deviations from Δ ($\Delta = 0$ in the ideal case, see Appendix) are less than 1 l mol^{-1} cm^{-1} ($\equiv$ 0·008 absorbance units) for spectra recorded above 110 °C (Table 2). The corresponding deviations from β_T of 3—6% are larger than normal—in our experience, less than 3% [17]—but for the above reasons these deviations are acceptable and the spectra above 110 °C internally linear. An increase in the deviations from β_T and Δ below this temperature are attributed to the larger extrapolations involved in calculating β_T and the appearance of the species $[NiCl(dmso)_5]^+$.

TABLE 3

Results obtained in the evaluation of ΔH from internal linearity analysis for the reaction $[NiCl_2(dmso)_4]^0 + Cl^- \rightleftharpoons [NiCl_3(dmso)]^-$ in dmso at Cl/Ni ratio 4·45

10^3T/K	Fraction [b] octahedral species (%)	Concentration/mol l^{-1} × 10^3			K_2'/l mol^{-1}
		$[NiCl_2(dmso)_4]^0$	$[NiCl_3(dmso)]^-$	Free Cl$^-$	
3·400	95·9 [c]	8·76	0·371	21·9	1·93
3·321	95·2	8·63	0·434	21·8	2·31
3·174	94·2	8·43	0·517	21·4	2·87
3·018	90·8	8·00	0·813	20·8	4·89
2·922	85·7	7·47	1·25	20·1	8·32
2·822	76·9	6·62	1·99	19·1	15·7
2·739	67·8	5·78	2·75	18·1	26·2
2·665	57·9	4·88	3·55	17·1	42·5
2·601	49·1	4·11	4·25	16·2	63·8
2·530	39·3	3·25	5·02	15·2	101
2·469 [a]	31·9	2·61	5·57	14·5	148
2·403	25·1	2·03	6·06	13·8	217
2·335	18·4	1·47	6·52	13·1	339
2·278 [a]	14·6	1·15	6·75	12·6	446
2·233	12·8	1·00	6·82	12·3	551

[a] Reference spectra. [b] $\beta_{oct} = -3{\cdot}93$, $\beta_{tet} = 1{\cdot}84$, $c_{oct} = (1{\cdot}84 - \beta_T)/5{\cdot}77$. [c] Corresponding $\beta_T = 3{\cdot}696$, other β_T values may be obtained, sequentially, from Table 2. ΔH Determined graphically as 52·2 kJ mol^{-1}.

(b) *Generation of terminal spectra.* When two reference spectra, from a set, are combined with chosen β values a spectrum is generated which, while belonging to the set, may not be experimentally recordable. The generated spectrum may correspond to a temperature above which the solution boils; at which one of the species dissociates or decomposes, or another equilibrium reaction dominates; or it may correspond to a temperature below which the reaction occurs, or the solution solidifies. If the correct choice of β is made the generated spectrum will correspond to one of the species participating in the equilibrium, free from any absorptions due to the other species. We denote such a spectrum the ' terminal ' spectrum, and there are naturally two terminal spectra for each two-species equilibrium. Hence the method of internal linearity has the potential of producing spectra not experimentally observable and of species not normally obtainable free from contributions due to related or decomposition products. Since for the present system the equilibrium is between an octahedral and a tetrahedral species we term the β values which generate the corresponding spectra β_{oct} and β_{tet}, respectively. Further details on the correct selection of terminal β values are given in the Appendix.

The spectrum of the octahedral species participating in the equilibrium was generated from the reference spectra. This spectrum, and another using a different β_{oct} value, are plotted in Figure 6.

β_{tet} Was estimated by determining values of β which would generate a tetrahedral profile with an absorption maximum at 16·00 kK of 100, 110, 120, 130, and 140 l mol^{-1} cm^{-1}. The respective values found were 1·28, 1·84, 2·40, 2·96, and 3·52 and the spectra generated from these β_{tet} values are compared in Figure 6.

(c) *Calculation of equilibrium quotients and enthalpy values.* A relationship exists between the concentrations of the species present in the equilibrium and β_{oct}, β_{tet}, and the various β values computed for all the internally linear spectra within a set. This relationship, derived in the Appendix, is

$$c_{oct} = (\beta - \beta_{tet})/(\beta_{oct} - \beta_{tet})$$

where c_{oct} is the fractional concentration of the octahedral species and β, β_{oct}, and β_{tet} are the internal linearity constants, all calculated relative to the same reference spectra. Thus the concentration of the octahedral and the tetrahedral species in solution at each temperature

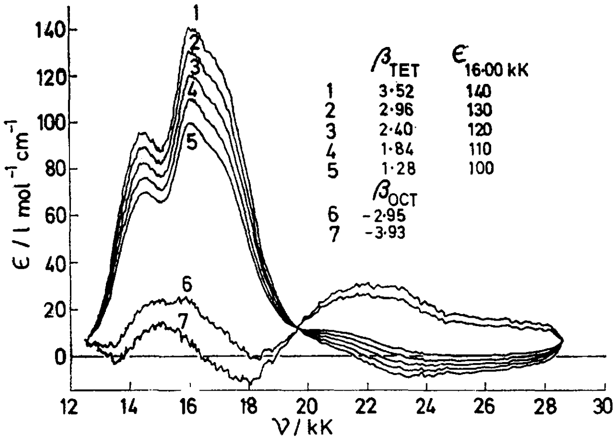

FIGURE 6 Generated spectra. Some spectra obtained on seeking the terminal spectra of $[NiCl_3(dmso)]^-$ and $[NiCl_2(dmso)_4]^0$ relative to spectra recorded at 132·1 and 166·0 °C for the system Ni^{II} + 4·45 Cl$^-$ in dmso

may be obtained, knowing the total concentration of nickel in solution. The concentration of free chloride may then be calculated and from the equation of the equilibrium reaction the equilibrium quotient K_2' was evaluated at each temperature studied. The enthalpy of the reaction (ΔH) was then obtained from the gradient of the plot of $\log_{10}(K_2')$ against $1/T$. A family of ΔH plots, using the above five β_{tet} values and $\beta_{oct} = -3{\cdot}93$, was obtained and is shown in Figure 5b. The plots are remarkably similar to those resulting from the conventional analysis (Figure 5a). The best fit to a linear plot was given by $\varepsilon_{16.00\,kK} = 110\,l\,mol^{-1}\,cm^{-1}$, with an equivalent gradient of 52·2 kJ mol^{-1}.

TABLE 4

Comparison of K_2' and ΔH values for nickel(II) + chloride in dmso.
K_2' (l mol^{-1}) for $[NiCl_2(dmso)_4]^0 + Cl^- \rightleftharpoons [NiCl_3(dmso)]^-$

	Conventional analysis	Internal linearity analysis [b] (ε = 110)		Conventional analysis by Griffiths and Scarrow [1]	
t/°C	(ε = 110 [a])	A	B	(ε = 128 [c])	(ε = 100 [d])
21·1	2·04	1·93	2·15		
28·3	2·07	2·31	2·28		
42·1	2·60	2·87	2·76		
58·4	4·74	4·89	4·79		
63·0				2·26	2·95
69·2	8·29	8·32	8·48		
72·9				4·07	5·36
81·3	15·9	15·7	16·1		
81·9				6·52	8·86
91·0				10·3	14·5
92·1	27·2	26·2	27·6		
97·8				14·1	20·6
102·3	45·1	42·5	45·2		
108·4				21·2	33·3
111·4	67·8	63·8	68·9		
122·2	107	101	111		
122·5				34·6	61·7
132·1	158	148	166		
133·6				46·7	95·3
142·1				56·7	132
151·5				69·2	190
155·2	369	339	407		
160·0				86·4	316
166·0	485	466	617		
174·9	545	551	723		
ΔH/kJ mol^{-1}	53·9 ± 1	52·2 ± 1	54·2 ± 1	55·6 ± 1·5	54·2 ± 1·5

[a] Using $\varepsilon_{16.00\,kK} = 110$ for $[NiCl_3(dmso)]^-$. [b] Internal linearity analyses: A, using reference spectra at 132·1 and 166·0 °C; B, using reference spectra at 81·3 and 111·4 °C. [c] K_2' Results from ref. 1, where $\varepsilon_{16.00\,kK} = 128$ was used. [d] Recalculation of K_2' from ref. 1. data using $\varepsilon_{16.00\,kK} = 100$.

The values for the equilibrium quotients calculated for this plot are listed in Table 3.

The entire analysis was repeated relative to reference spectra recorded at 81·3 and 111·4 °C, in order to investigate the effect of choosing one and possibly both reference spectra outside the temperature range of the two-species equilibrium. Larger deviations in the internal linearity constants were obtained and the ΔH plots were less linear than those from the above analysis. A best fit to $\varepsilon_{16.00\,kK} = 111\,l\,mol^{-1}\,cm^{-1}$ gave a gradient equivalent to 54·3 kJ mol^{-1}.

DISCUSSION

The equilibrium quotients calculated by the methods of analysis described above are compared with the earlier data[1] in Table 4. There is good overall agreement between the values of K_2' calculated by the conventional analysis and by the internal linearity method relative to the reference spectra at 132·1 and 166·0 °C. However, for temperatures above 130 °C the equilibrium quotients from the internal linearity method relative to spectra recorded at 81·3 and 111·4 °C differ significantly from the other analyses. This is due to the presence of a third species at the lower temperature. We conclude that, provided a range of temperatures can be established over which a two-species equilibrium exists, the internal linearity and conventional methods of ΔH determination give identical results within experimental error.

Large differences result when comparing the equilibrium quotients calculated from a maximum molar absorbance for $[NiCl_3(dmso)]^-$ of 110 l mol^{-1} cm^{-1} used in this study with those from the value of 128 l mol^{-1} cm^{-1} used previously.[1] The data of Griffiths and Scarrow[1] has been recalculated making no assumptions about this molar absorbance. A linear ΔH plot was fitted to $\varepsilon_{16.00\,kK} = 100\,l\,mol^{-1}\,cm^{-1}$, and from the gradient the enthalpy corresponded to 54·2 kJ mol^{-1}. The recalculated equilibrium quotients are in somewhat closer agreement with those from the present study (Table 4), but it is noted that the earlier work used higher chlorine/nickel mole ratios (between 4·87 and 9·65; this work, 4·45) and, more important, in the earlier work the spectra were not corrected for the thermal expansion of dmso, a factor which must be significant over a temperature range of 140 °C.

A comparison of the ΔH values determined by each analysis listed in Table 4 shows that the enthalpy of the reaction

$$[NiCl_2(dmso)_4]^0 + Cl^- \longrightarrow [NiCl_3(dmso)]^-$$

observed in dmso over the temperature range 110—175 °C is 54 ± 1 kJ mol^{-1}. However the ΔH plots are linear over a wider temperature range than that established for the two-species equilibrium. Slight changes in the spectra of the species with temperature change may be involved, but this could also arise from the analyses being independent of the nature of the octahedral species participating in the equilibrium at lower temperatures. This suggests that the value of ΔH represents mainly the enthalpy of the configurational change from octahedral to tetrahedral, irrespective of the number of chloride ions exchanged in the equilibrium. The enthalpy reported for exchanging a chloride ligand on nickel for a solvent molecule, without configurational change, has varied [6,18] between 2·5 and 17·2 kJ mol^{-1}, and the configurational change has been estimated [18,19] as 32·6 kJ mol^{-1}.

It is concluded that a new method has been established for determining enthalpy values. Further, the application of fourth derivative analyses to spectra enabled the species present, and the temperature ranges in which they were in significant concentration, to be determined with certainty. As a consequence, ΔH was determined with increased precision and confidence. It is also concluded that computer-calculated derivative spectra can be used to great advantage when investigating multi-specie systems.

APPENDIX

Digitization of Spectra.—A spectrum is most simply digitized by recording both the absorbance and the wavelength (or wavenumber as appropriate) at suitable, though not necessarily equal, intervals of wavelength. By this means, each digitized point is accurately defined on both the x and y axes. It is however more useful and economical to record at *equal* intervals of wavelength. The bulk of the data then required to represent a spectrum is approximately halved as the wavelength corresponding to every digitized wavelength need not be stored. If (i) the initial wavelength of digitization, (ii) the wavelength interval, and (iii) the total number of digitized absorbances are known, then the wavelength corresponding to any sequentially digitized absorbance can be assigned. Perhaps the most important advantage of digitizing spectra at equal wavelength intervals is the simplicity with which a variety of mathematical procedures (such as smoothing or differentiating spectra) may be applied to such data.

Fourth Derivative Spectra.—A digitized spectrum may be completely resolved into its component bands from a knowledge of the first four derivative functions of that spectrum. Morrey [20] has thereby resolved overlapping Gaussian, Cauchy, and Student T_3 distributions; an analysis of these derivatives enabled all the band parameters to be determined. The method requires no assumption about the type of distribution involved.

Second and fourth derivative curves reach minimum and maximum values respectively at, or close to, wavelengths corresponding to the maximum absorbance of the component bands in a spectrum. In practice the precision of this method for locating peak maxima is dependent upon many factors, including the number of data points used to define the spectrum and the mathematical technique employed. For example, fourth-derivative curves obtained by a convolution procedure [21] of a synthesized curve will contain the correct number of peaks, but because each component band has become broadened by the convolution procedure the observed derivative curve does not always contain sharp bands. The observed peak maxima are thus often displaced from the true maxima of the (known) component bands.[22] We have therefore used a technique for obtaining derivative curves which does not involve any smoothing of the data, the method of differences. It may be argued that this method is not a sophisticated mathematical method and that we are not fully optimizing the data we have available but, used with circumspection, striking resolutions can be achieved. Butler and Hopkins [23] pioneered this technique and successfully obtained the original peak maxima from extensively overlapping synthesized spectra of Gaussian and Cauchy functions. They found in all the examples studied that, on using their technique to obtain second- and fourth-derivative curves, the fourth-derivative curve gave the better resolution for peak maxima.

Summarized, the method is as follows. If $A(n)$ is the absorbance at the nth wavelength of an equidistantly digitized spectrum, and a, b, c, and d are integers such that $A(n + a)$ is the absorbance at the $(n + a)$th wavelength, *etc.*, then a function linearly related to the first derivative (A^{I}) may be determined from the expression:

$$A^{\mathrm{I}}(n + a/2) = A(n + a) - A(n) \qquad (1)$$

By successively differentiating this expression the fourth derivative (A^{IV}) may be obtained as:

$$\begin{aligned} A^{\mathrm{IV}}(n + (a + b + c + d)/2) = {} & A(n + a + b + c + d) \\ & - [A(n + a + b + c) + A(n + a + b + d) + \\ & A(n + a + c + d) + A(n + b + c + d)] \\ & + [A(n + a + b) + A(n + a + c) + A(n + a + d) + \\ & A(n + b + c) + A(n + c + d) + A(n + b + d)] \\ & - [A(n + a) + A(n + b) + A(n + c) + A(n + d)] + \\ & A(n) \end{aligned} \qquad (2)$$

Butler and Hopkins [24] found that the values of the integers a, b, c, and d which generated the most noise-free derivative spectra differed by either 1,1 and 2 or 2,1 and 1. We have confirmed their findings in this respect and have established that a trial and error method must be employed to establish the best value of a to be used. No general rules can be given, the choice depends upon the total number of data points used to describe the spectrum,

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and, to some extent, the shape of the profile to be differentiated.

Certain principles have however become apparent. There is, for example, a reciprocal relationship between noise and resolution in fourth-derivative curves obtained by this method. Using small values of a the amount of noise present is large, but as a is increased the noise decreases and the resolved bands become sharper. However, if a is increased further the resolved bands broaden, overlap, and peak maxima are then difficult to determine. There is, however, a fairly wide range of a values over which relatively noise free and sharp bands are obtained, and in which the positions of the resolved maxima are independent of the integer set. Hence the method gives consistent results, but the acceptable range of a values must be established for a set of spectra.

Internally Linear Spectra.—If a two-species equilibrium is present in solution, and the total concentration of the two absorbing and interacting species remains constant while their relative concentrations are altered by some applied constraint, then the spectra recorded, which will normally contain at least one isosbestic point, will be internally linear. That is, any one *spectrum* in an internally linear set is a linear combination of any other two spectra from that set. This may be expressed mathematically as:

$$\varepsilon_3 = (1 - \beta)\varepsilon_1 + \beta\varepsilon_2 \quad (3)$$

This equation is valid at any wavelength within the internally linear range. ε_1, ε_2, and ε_3 Are the formal absorbances of three spectra at any wavelength; β is the constant of internal linearity relative to the spectra ε_1 and ε_2. The formal absorbance is calculated relative to the total concentration of absorbing species. The symbol β is an abbreviation of $\beta_{(3,2,1)}$, which specifies the order in which spectra appear in equation (1) and ε_1 and ε_2 are termed the reference spectra.

Rearrangement of equation (1) gives

$$\beta_\lambda = (\varepsilon_3 - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1) \quad (4)$$

β_λ implying that the constant of internal linearity (β) is computed at each digitized wavelength. An average value ($\bar{\beta}$) is then calculated from the array of β_λ values determined at each wavelength. If a meaningful $\bar{\beta}$ is found, the deviation (Δ_λ) from ideal linearity ($\Delta_\lambda \longrightarrow 0$) is computed at each wavelength from:

$$\Delta_\lambda = (1 - \bar{\beta})\varepsilon_1 + \bar{\beta}\varepsilon_2 - \varepsilon_3 \quad (5)$$

A plot of this deviation against wavelength will establish to what degree, and over what wavelength range the set of spectra can be considered internally linear.

Determination of Average β *Values.*—The previous procedure,[9] of deleting obviously unrealistic values before averaging β, is unsatisfactory. We have developed a more rigorous approach which, while not being completely rigorous, does eliminate the need for examining and making a judgment on each β_λ value in turn. From equation (4) it will be seen that if ε_1 and ε_2 have very similar values β_λ can be very large, or even change sign if noise in the spectra make ε_1 and ε_2 fortuitously cross over at some wavelengths. We therefore employed a gate: if the difference between spectra at any wavelength is less than a *threshold* value, the corresponding value of β_λ is considered insufficiently accurate to warrant further averaging and it is rejected. A suitable threshold difference is 0·01 absorbance units.

Other β_λ values are rejected if they lie outside a range defined about a preliminary averaged value, determined as follows. A value of $(\bar{\beta})_p$ is calculated for the data points remaining after passing the threshold gate and its r.m.s. value is also found. Any β_λ value then lying outside the range $(\bar{\beta})_p \pm$ r.m.s. $(\bar{\beta})_p$ is rejected, and from the remaining data the mean $\bar{\beta}$ is determined, together with its r.m.s. deviation. In general, the percentage r.m.s. deviation from $\bar{\beta}$ is around 2% for internally linear spectra which are dependent upon parameters such as composition of the solvent or pH; where temperature is the parameter the value is around 5%.

As a further check for a meaningful $\bar{\beta}$, it can be shown that if an incorrect value of $\bar{\beta}$ is obtained, Δ will be displaced from zero and will change markedly in value on traversing the wavelengths of the isosbestic points.

Generation of Spectra.—Consider a set of spectra describing a two-species equilibrium. From equation (3) it may be seen that if two experimental spectra (ε_1 and ε_2) are chosen as the two reference spectra, then a third spectrum (ε_3) may also 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 plotted and examined, a situation will be reached when the absorption due to one species is eliminated from the generated spectrum. A value of β is thus obtained which will generate the ' terminal ' spectrum of one component species of the system relative to the reference spectra. If β is changed even further meaningless spectra will result, for example, largely negative absorbances.

Relationship between β *and the Equilibrium Quotient.*—Consider an equilibrium between two species in solution, $A \rightleftharpoons B$, where (i) A and B are the only absorbing species in the wavelength region studied; (ii) the total concentration, $c_T = c_A + c_B$, 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_{A1} and c_{B1} are the concentrations of A and B at temperature 1, *etc.*; ε_A and ε_B are the molar absorptions of the individual species of A and B at the wavelength under consideration; and ε_1 is the formal absorbance of the equilibrium system at temperature 1, *etc.*, at that wavelength, then assuming the law of additive absorptions and unit path length:

$$\varepsilon_1 = \varepsilon_A \cdot c_{A1} + \varepsilon_B \cdot c_{B1}$$

This may be rewritten as

$$\varepsilon_1 = (\varepsilon_A - \varepsilon_B)c_{A1} + \varepsilon_B \cdot c_T$$

and similar expressions may be obtained for ε_2 and ε_3, which can then be substituted into equation (4) to yield:

$$(\varepsilon_3 - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1) = (c_{A3} - c_{A1})/(c_{A2} - c_{A1}) = \beta_{(3,2,1)} \quad (6)$$

This relationship may now be made quantitative on generating the ' terminal ' spectra of the component species A and B.

If β_A and β_B are the values of β which generate the individual spectra of A and B relative to the reference spectra, recorded at temperatures 1 and 2 [such that $\beta_A = \beta_{A,2,1} = (\varepsilon_A - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1)$], then when $\beta = \beta_A$, $c_{A3} = c_T$, since the spectrum of A results from the conversion of all the absorbing species to A. Similarly, when $\beta = \beta_B$, $c_{A3} = 0$ as there is no contribution from the spectrum of A to the generated spectrum of species B. Hence equation (6) becomes:

$$c_{A_3}/c_T = (\beta - \beta_B)/(\beta_A - \beta_B) \qquad (7)$$

This equation defines the linear relationship between the fractional concentration of one component of a two-species equilibrium (c_{A_3}/c_T) and the internal linearity constants β, β_A, and β_B, all calculated relative to the same reference spectra. Knowing the total concentration of A and B in the system, c_T, the concentration of A and B individually in solution at each temperature may be found from equation (7), *i.e.* using a β value calculated, 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, since for one reference spectrum β will be 1 and 0 for the other. The enthalpy of the reaction (ΔH) is then obtained from the van't Hoff isochore ($d(\ln K)/d(1/T) = -\Delta H/R$. Standard thermodynamic parameters cannot be calculated unless the activities of the species are known.

ΔH from Internal Linearity Theory: Some Comments.—(i) The most important advantage of, and indeed the reason for developing this method of determining ΔH values, is that it does *not* depend on the existence of a wavelength region in the set of spectra where only one species absorbs light, the requirement of conventional methods. (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. In addition, the method is efficient, one equilibrium quotient being calculated for each internally linear spectrum in a set greater than three. (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 as follows. (*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 of the method if it is to be applied to stepwise reactions. If more than two species contribute to the measured absorption, the mathematical derivation cannot be simplified to equation (6). If three species absorb, and there is a simple relationship between two of them, then equation (6) can sometimes be attained, and the system is treated as a pseudo-two-species equilibrium.[17]

(*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 practise, 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 explains the earlier remark that the percentage r.m.s. deviation of $\bar{\beta}$ of around 5% is acceptable for temperature dependent equilibria, whereas equilibria dependent on other external parameters are expected to have deviations of around 2%.

(*c*) Ultimately, thermodynamic data are determined from van't Hoff's 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 solutions studied here will be linear over the restricted temperature ranges used.

Clearly, significant restrictions are placed upon the calculation of thermodynamic data from internal linearity theory—but the conventional method used in this and the earlier paper [1] involve similar restrictions.

Recognition of Terminal Spectra.—This is not always a simple procedure. Our experience suggests that while certain guide-lines may be laid down each system must be viewed initially as a special case.

Obviously if too great a value of β is used in generating a spectrum a partially negative profile will result. However, it is not correct to assume that the terminal β value has been reached when the generated spectrum has zero absorbance at one (or more) wavelengths. We found that it was better to employ the criterion that the generated spectrum should have an *average* absorption of zero in the region where the other species, whose absorbance was being removed, was known to absorb. Alternatively, β can be altered until a known and expected feature in the spectrum of the species is attained.[25]

It is sometimes possible to know the oscillator strength of the species. Under these circumstances the various generated spectra are plotted on paper, carefully cut out and weighed, and compared with the weight of a spectrum having the required oscillator strength.[17]

In theory, the generated profile for one species only will have a smooth outline, free from small variations due to small amounts of the other species: in practise, the generated spectrum has superimposed the noise inherent in the system multiplied approximately by the value of β used. We are currently evaluating suitable computer procedures for smoothing the noise from such spectra, and when this has been accomplished the application of the very sensitive fourth-derivative analyses to such curves is expected to pin-point the β value at which the contribution to the spectrum by the other species just disappears.

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