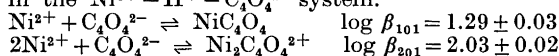


The Stability Constants for Complexes between Nickel(II) and Squaric Acid

DAGMAR ALEXANDERSSON and NILS-GÖSTA VANNERBERG

*Department of Inorganic Chemistry, Chalmers University of Technology and the
University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden*

The formation of complexes between nickel(II) and squaric acid has been studied at 25°C with spectrophotometric methods in solutions in which the total molarity was held constant at 3 M by the addition of NaClO₄. The total concentrations of nickel perchlorate and sodium squarate ranged from 0 to 600 mM and 0.1 to 3 mM, respectively. The pH range was 1.3–5.0. Preliminary constants were obtained graphically and were then refined with the generalized least squares program Letagrop. The experimental data could best be explained in terms of the following equilibria and corresponding stability constants in the Ni²⁺–H⁺–C₄O₄²⁻ system:



The errors given correspond to an error of 3σ in β, where σ is the standard deviation in β.

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, H₂C₄O₄) was not known until 1959, when it was first synthesized by Cohan *et al.*¹ The aromatic character of the anion, A²⁻, its stability and its solubility in water have, since then, stimulated a number of investigations on the acid and its metal complexes. A survey of reported values for the acidity constants at varying ionic strength has been given previously.² Recently acidity constants have been reported by Gelb³ (pK_{a1} = 0.51) and by Schwartz and Howard^{4,5} (pK_{a1} = 0.5 and pK_{a2} = 3.48).

Schwartz and Howard carried out conductance measurements as well as potentiometric titrations, while Gelb measured conductometrically. They all worked with varying ionic strength and used calculated activity coefficients to determine the thermodynamic acidity constants.

The formation of squarate complexes with metal ions has been studied by Tedesco and Walton,⁶ who determined formation constants for iron(III), uranium(VI), aluminium(III), copper(II), manganese(II), cobalt(II), and nickel(II), and by Cilindro *et al.*⁷ who studied complex formation with some

actinides. In their investigation of nickel(II) squarate complexes, Tedesco and Walton used a paper chromatographic method with 0.5 M NaClO₄ as supporting electrolyte. The pH range was 3.5–4 and the temperature 25°C. Only a preliminary constant was thus obtained. In connection with our work on squaric acid and its complex formation with transition metal ions a more exhaustive investigation was desirable.

EXPERIMENTAL

Chemicals and analyses. Nickel(II) perchlorate was prepared from nickel carbonate (BDH) and perchloric acid (Merck *p.a.*). The nickel perchlorate was recrystallized several times by dissolving in hot water, cooling and filtering off the precipitated crystals. The nickel perchlorate solution was standardized against a standard EDTA solution, using murexide as indicator according to Vogel.⁸ The EDTA solution was prepared from Titrplex III (Merck *p.a.*) by dissolving a weighed amount of the salt. The EDTA concentration was checked with a zinc chloride solution, prepared from zinc sticks (Merck *p.a.*) and hydrochloric acid (Merck *p.a.*), as described by Vogel.⁹

The free hydrogen ion concentration in the nickel perchlorate solution was determined by Gran methods.¹⁰

Perchloric acid, sodium perchlorate, and sodium squarate were prepared and analyzed as described elsewhere.²

Apparatus. The ultra-violet absorption measurements were performed on a Gilford 240 spectrophotometer. Matched quartz cells of path lengths 0.01, 0.05, 0.1, 0.2, 0.5, and 1 cm were employed, these being calibrated before use. During the measurements, the sample compartment was thermostated to 25.0 ± 0.1°C.

The solutions to be investigated were prepared by mixing solutions of nickel(II) perchlorate, sodium squarate and perchloric acid, the total molarity being held constant at 3 M by addition of sodium perchlorate. The total concentrations of sodium squarate, *A*, and nickel perchlorate, *B*, varied within the ranges 0.1–3 mM and 0–600 mM, respectively. The concentration of the free squarate ion, *a*, ranged, however, from 0.004 to 1 mM, owing to the varying hydrogen ion and nickel ion concentrations. The variation is limited by the slight solubility of squarates and by their high molar absorptivities. The free hydrogen ion concentration, *h*, was measured in each solution by emf methods as is described previously.² The sodium perchlorate concentration was then 3.000 M – 2*A* – 2*B* – *h*.

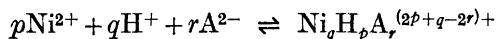
No nickel hydroxide complexes were formed, according to calculations using the formation constants for nickel(II) hydroxide complexes, determined by Burkov *et al.*¹¹

The absorbance was measured at 26 wavelengths ranging from 220 to 290 nm. Sixteen of these absorbances corresponding to wavelengths ranging from 240 to 270 nm were used in the calculations. The stability of the sodium squarate solutions as well as of the nickel squarate solutions is good. For some solutions the absorbances were measured again after 6–9 months and found to have changed only by 1–2 %.

LIST OF SYMBOLS

<i>A</i>	total concentration of squaric acid, H ₂ A
<i>a</i>	free concentration of squarate ions, A ²⁻
<i>B</i>	total concentration of nickel ions, Ni ²⁺
<i>b</i>	free concentration of nickel ions, Ni ²⁺
<i>H</i>	total concentration of hydrogen ions, H ⁺
<i>h</i>	free concentration of hydrogen ions, H ⁺
<i>c_{pqr}</i>	free concentration of Ni _{<i>p</i>} H _{<i>q</i>} A _{<i>r</i>} , ^{(2<i>p</i>+<i>q</i>-2<i>r</i>)+}
<i>A_s</i>	absorbance
<i>l</i>	optical pathlength

ε apparent molar absorptivity
 β_{pqr} equilibrium constant for the reaction



defined so that

$$c_{pqr} = \beta_{pqr} b^p h^q a^r$$

ε_{pqr} molar absorptivity for the complex $\text{Ni}_p\text{H}_q\text{A}_r^{(2p+q-2r)+}$
 v_0, A_0, H_0 volume and total concentrations in the starting solution in the emf measurements
 v_t, A_t, B_t, H_t volume and total concentrations in the solution added in the emf measurements
 E potential

SPECTROPHOTOMETRIC MEASUREMENTS

Squaric acid and its anions show strong absorption of radiation in the ultra-violet but not in the visible range. Nickel squarates also absorb in the ultra-violet region but the absorbance of nickel perchlorate is very weak. In this work the variation of the absorbance with changes in the concentrations of

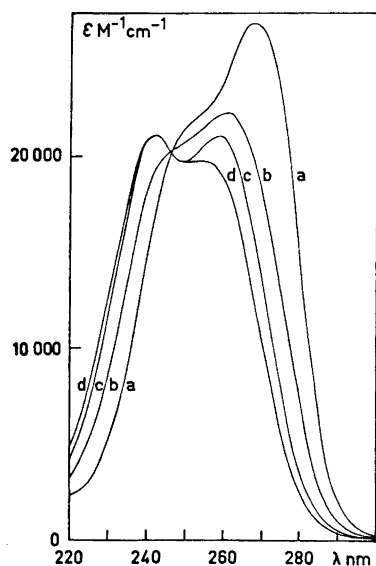


Fig. 1. ε data as a function of γ for sodium squarate solutions with different hydrogen ion concentrations. The measurements were made every 2nd nm, all points falling on the curves. The following values for $-\log h$ were used: a. 6.21; b. 3.31; c. 2.06; d. 1.08.

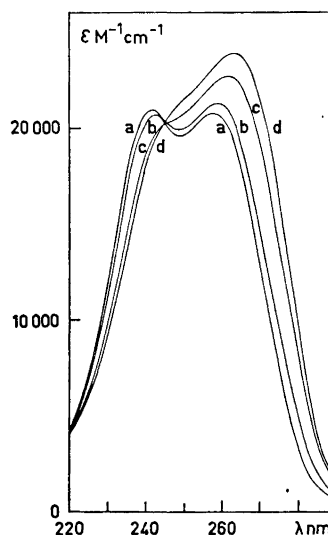


Fig. 2. ε data as a function of λ for solutions with $A = 0.1201$ mM and different nickel perchlorate concentrations. The following values for B and $-\log h$ were used: a. 0 mM and 2.03; b. 85.18 mM and 2.00; c. 352.4 mM and 1.93; d. 598.6 mM and 1.86.

the components has been used to determine the stability constants of the complexes. Spectra were registered for solutions of sodium squarate with varying h values (*cf.* Fig. 1) and for solutions containing both sodium squarate and nickel perchlorate. The absorbances of series of solutions with pH 2 and pH 5, respectively, are shown in Figs. 2. and 3. According to determinations made previously² the HA^- anion dominates the squaric acid system at pH 2 while the A^{2-} anion dominates at pH 5 (*cf.* Fig. 4).

When the nickel perchlorate concentration is varied from 0 to 100 mM at pH 5 and the sodium squarate concentration is kept constant, the absorbances change only slightly (*cf.* Fig. 3). This may either be due to the fact that the complexes formed have about the same molar absorptivities as the squarate ion, A^{2-} , or that complex formation is negligible.

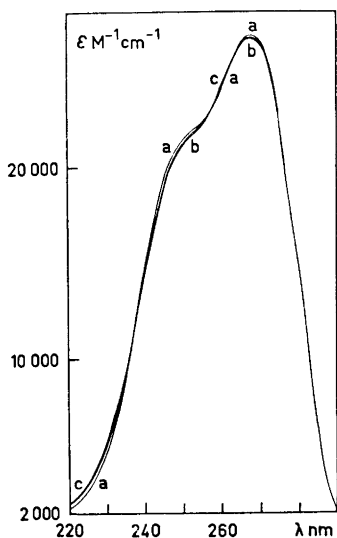


Fig. 3. ϵ data as a function of λ for solutions with $A = 1.000$ mM and different nickel perchlorate concentrations. The following values for B and $-\log h$ were used: a. 0 mM and 4.96; b. 60.00 mM and 5.01; c. 100.0 mM and 4.95.

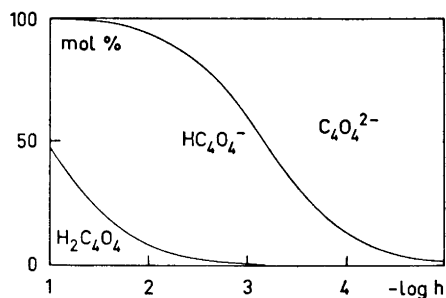


Fig. 4. The distribution of complexes as a function of $-\log h$ for squaric acid.

The change in absorbance is more pronounced in solutions with pH 2 (*cf.* Fig. 2). Nickel complexes would therefore appear to be formed at this pH.

TREATMENT OF THE DATA

The absorbance, A_s , may be expressed:

$$A_s = \epsilon l A = l \sum_p \sum_q \sum_r \epsilon_{pqr} c_{pqr} \quad (1)$$

Inserting the expression

$$c_{pqr} = \beta_{pqr} b^p h^q a^r$$

in eqn. (1) gives

$$\varepsilon = \frac{\sum_p \sum_q \sum_r \varepsilon_{pqr} \beta_{pqr} b^p h^q a^r}{\sum_p \sum_q \sum_r r \beta_{pqr} b^p h^q a^r} \tag{2}$$

I. $p = 0$. In solutions where no nickel is present

$$\varepsilon = \frac{\varepsilon_{001} + \varepsilon_{011} \beta_{011} h + \varepsilon_{021} \beta_{021} h^2}{1 + \beta_{011} h + \beta_{021} h^2} \tag{3}$$

The constants β_{011} and β_{021} have been determined earlier by means of emf methods at the same ionic strength,² *i.e.* $\log \beta_{011} = 3.19 \pm 0.001$ and $\log \beta_{021} = 4.15 \pm 0.02$, the errors given corresponding to an error of 3σ in β . Using these values of the constants, the experimental data from solutions not containing nickel were processed with the spectrophotometric version of the "Letagrop" program.¹² When β_{011} was varied together with ε_{001} , ε_{011} , and ε_{021} for the 16 wavelengths, $\log \beta_{011} = 3.13 \pm 0.05$ was obtained as "the best value". The β values calculated from the emf measurements were used in the following, since these are the most accurate values. The ε values calculated holding these β values constant are given in Table 1 and used in the following.

Table 1. Molar absorptivities, ε_{pqr} , in $M^{-1} \text{ cm}^{-1}$ calculated with the Letagrop program. The errors are given as 3σ where σ is the standard deviation in ε .

$\lambda \text{ nm}$	ε_{021}	ε_{011}	ε_{001}	ε_{101}	ε_{201}	ε_{100}
240	20 800 ± 470	21 100 ± 120	14 800 ± 140	13 100 ± 560	16 300 ± 310	0.011
242	21 100 ± 440	21 400 ± 120	16 900 ± 120	15 000 ± 510	18 000 ± 260	0.011
244	21 000 ± 460	20 900 ± 120	18 600 ± 130	17 100 ± 330	19 400 ± 180	0.011
246	20 800 ± 470	20 200 ± 120	20 000 ± 140	18 600 ± 310	20 600 ± 160	0.010
248	20 500 ± 450	19 700 ± 120	20 900 ± 130	19 900 ± 360	21 500 ± 200	0.010
250	20 200 ± 440	19 600 ± 110	21 500 ± 130	20 600 ± 310	22 200 ± 210	0.010
252	19 900 ± 380	19 800 ± 100	21 900 ± 110	21 100 ± 320	22 700 ± 210	0.009
254	19 300 ± 380	20 300 ± 100	22 200 ± 110	21 400 ± 300	23 100 ± 210	0.009
256	18 600 ± 390	20 800 ± 100	22 600 ± 110	21 900 ± 350	23 600 ± 230	0.009
258	17 500 ± 420	21 100 ± 110	23 200 ± 120	22 600 ± 370	24 300 ± 240	0.009
260	16 100 ± 450	21 000 ± 120	24 100 ± 130	23 600 ± 400	25 000 ± 260	0.009
262	14 600 ± 540	20 400 ± 140	25 100 ± 160	24 700 ± 470	25 600 ± 300	0.009
264	12 800 ± 650	19 300 ± 170	26 100 ± 190	25 700 ± 500	26 100 ± 370	0.009
266	10 900 ± 760	17 700 ± 200	26 800 ± 220	26 400 ± 490	26 300 ± 370	0.008
268	9 000 ± 940	15 600 ± 250	27 200 ± 270	26 700 ± 510	26 000 ± 360	0.008
270	7 000 ± 1080	13 400 ± 280	26 900 ± 320	26 500 ± 450	25 300 ± 400	0.007

II. $q = 1$. In eqn. (1) $\text{Ni}_p \text{H}_q \text{A}_r^{(2p+q-2r)+}$ represents the general form for a nickel complex. In the pH range 1.3–5 it is, however, probable that not more than one hydrogen ion is bound per complex. The total concentration of squaric

acid is rather low, $A \leq 3$ mM so that $r=1$ seems to be most likely. Neglecting the weak absorbance of the nickel ions (*cf.* Table 1) eqn. (2) is reduced to the form

$$\varepsilon = \frac{\varepsilon_{001} + \varepsilon_{011}\beta_{011}h + \varepsilon_{021}\beta_{021}h^2 + \sum_p \varepsilon_{p11}\beta_{p11}b^p h + \sum_p \varepsilon_{p01}\beta_{p01}b^p}{1 + \beta_{011}h + \beta_{021}h^2 + \sum_p \beta_{p11}b^p h + \sum_p \beta_{p01}b^p} \quad (4)$$

or

$$\begin{aligned} & [\varepsilon(1 + \beta_{011}h + \beta_{021}h^2) - (\varepsilon_{001} + \varepsilon_{011}\beta_{011}h + \varepsilon_{021}\beta_{021}h^2)] / \varepsilon b = \\ & = - \sum_p b^{p-1}(\beta_{p11}h + \beta_{p01}) + \sum_p b^{p-1}(\varepsilon_{p11}\beta_{p11}h + \varepsilon_{p01}\beta_{p01})\varepsilon^{-1} \end{aligned} \quad (5)$$

In order to investigate whether the complexes $\text{Ni}_p\text{HA}^{(2p-1)+}$ were present, all other nickel complexes were neglected and all terms in eqn. (5) divided by a factor h . Data from solutions with $A = 1.157$ mM, $B = 500.0$ mM and pH varying from 1.3 to 3.7 were then inserted. Since $B \gg A$, b can be replaced by B . All quantities on the left-hand side of the equation are then known and the coefficient for the term ε^{-1} , $\sum_p B^{p-1} \varepsilon_{p11}\beta_{p11}$, is constant. The left-hand side of the equation was plotted against ε^{-1} , (*cf.* Fig. 5) to test whether or not there was a linear correlation. It was obvious that there was no linear correlation $\text{Ni}_p\text{HA}^{(2p-1)+}$ thus not being the main complexes formed.

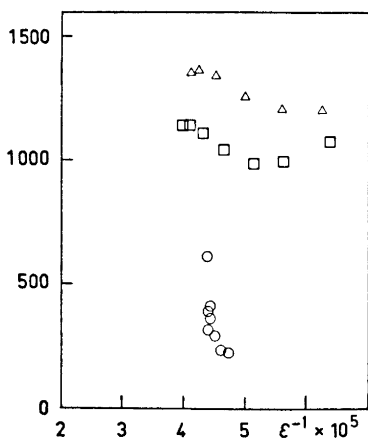


Fig. 5. The left-hand side of eqn. (5) divided by h , as a function of ε^{-1} for different wavelengths. $A = 1.157$ mM, $B = 500.0$ mM and the values for λ are \circ 254 nm, \square 268 nm and \triangle 270 nm.

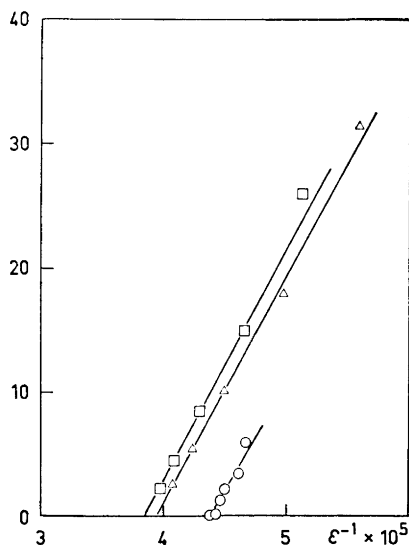


Fig. 6. The left-hand side of eqn. (5) as a function of ε^{-1} for different wavelengths. $A = 1.157$ mM, $B = 500.0$ mM and $1.3 \leq -\log h \leq 3.7$. The λ values are \circ 254 nm, \square 268 nm and \triangle 270 nm. From the slope and intercept for $\lambda = 270$ nm $\sum_p \beta_{p01}b^{p-1} = 72 \text{ M}^{-1}$ and $\varepsilon_{101} = 25\,300 \text{ M}^{-1} \text{ cm}^{-1}$ are obtained.

III. $q = 0$. The complexes $\text{Ni}_p\text{HA}^{(2p-1)+}$ were then neglected and the complexes $\text{Ni}_p\text{A}^{(2p-2)+}$ tested by inserting the same data in eqn. (5) (*cf.* Fig. 6). This time a linear correlation was obtained. The complexes $\text{Ni}_p\text{A}^{(2p-2)+}$ must therefore be present both in solutions with pH 2 and in those with pH 5. From Fig. 3 it is seen that these complexes have molar absorptivities which differ little from that of the squarate ion, ϵ_{001} . Supposing all $\epsilon_{p01} \approx \epsilon_{101}$, the slope and intercept of the line give

$$\sum_p \beta_{p01} B^{p-1} = 72; \quad \epsilon_{101} = 25\,300$$

for $\lambda = 270$ nm.

Data from solutions with pH 2 and varying A and B values were then used for the wavelength $\lambda = 270$ nm. In Fig. 7 the left-hand side of eqn. (5) has been plotted against ϵ^{-1} . If NiA is supposed to be the only nickel complex present, the slope and intercept of the line give

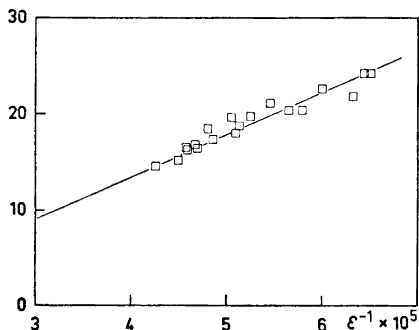


Fig. 7. The left-hand side of eqn. (5) as a function of ϵ^{-1} for $\lambda = 270$ nm, different A and B values and pH ~ 2 . From the slope and intercept $\beta_{101} = 4 \text{ M}^{-1}$ and $\epsilon_{101} = 108\,000 \text{ M}^{-1} \text{ cm}^{-1}$ are obtained.

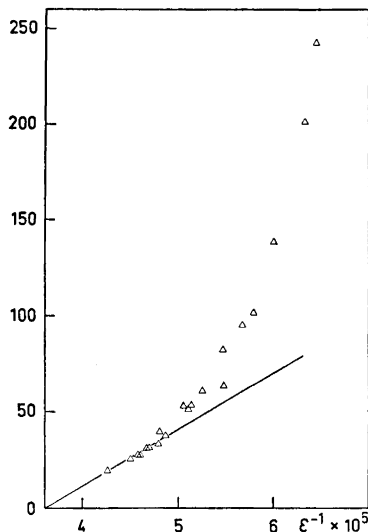


Fig. 8. The left-hand side of eqn. (5) divided by a factor B , as a function of ϵ^{-1} for $\lambda = 270$ nm, different A and B values and pH ~ 2 . From the slope and intercept $\beta_{201} = 107 \text{ M}^{-2}$ and $\epsilon_{201} = 27\,600 \text{ M}^{-1} \text{ cm}^{-1}$ are obtained.

$$\beta_{101} = 4; \quad \epsilon_{101} = 108\,000$$

The ϵ_{101} value obtained seemed to be too high compared to $\epsilon_{001} = 26\,900$. To test whether or not the complex Ni_2A^{2+} was formed, all terms in eqn. (5) were divided by a factor B and the left-hand side of the new equation was plotted against ϵ^{-1} (*cf.* Fig. 8). If all nickel complexes except Ni_2A^{2+} were neglected and data from solutions with the highest B values (and thus the highest ϵ values) were used, then

Table 3. Survey of the results from the calculation of the β constants, I by graphical methods, II, III, and IV using the Letagrop program.

	Number of experi- mental ε values	β_{pqr} varied (pqr)	β_{pqr} constant (pqr) 021, 011 and	ε_{pqr} varied (pqr)	$\log(\beta_{pqr} \pm 3\sigma)$	$U \times 10^7$	$\sigma(\varepsilon)$
I. Fig. 9		101			1.28		
Fig. 8		201			2.03		
II. Different	138	101		101	1.89 ± 0.05	0.71	240
h values	138	201		201	2.20 ± 0.05	0.71	240
A and B	138	111		111	2.80 ± 0.14	6.0	700
constant	138	122		122	8.83 ± 0.23	7.1	770
III. Different	656	101		101	1.61 ± 0.02	9.7	420
A and B	656	201		201	2.23 ± 0.02	5.2	290
values	656	301		301	2.78 ± 0.04	12	450
	656	102		102	5.70 ± 0.05	95	1280
IV. II+III	772	{ 101		101	1.27 ± 0.07	2.53	185
		{ 201		201	2.05 ± 0.05		
	182	101	201	101	1.32 ± 0.05	0.44	163
	404	201	101	201	2.01 ± 0.03	1.29	183
	772	{ 101		—	1.29 ± 0.03	2.57	183
		{ 201		—	2.03 ± 0.02		

$$\beta_{201} = 107; \quad \varepsilon_{201} = 27\ 600$$

were obtained.

Since it seemed probable that both complexes were present in the solutions, eqn. (5) was re-written:

$$[\varepsilon(1 + \beta_{011}h + \beta_{021}h^2) - (\varepsilon_{001} + \varepsilon_{011}\beta_{011}h + \varepsilon_{021}\beta_{021}h^2)]/\varepsilon B - [(\varepsilon_{201} - \varepsilon)\beta_{201}B]/\varepsilon = -\beta_{101} + \varepsilon_{101}\beta_{101}\varepsilon^{-1} \quad (6)$$

and

$$\beta_{201} = 107; \quad \varepsilon_{201} = 25\ 300$$

were inserted. The ε_{201} value obtained when only one complex was supposed to be present is probably too large. A new plotting (*cf.* Fig. 9) gave

$$\beta_{101} = 19; \quad \varepsilon_{101} = 28\ 100$$

Compared to the result above $\sum_p \beta_{p01} b^{p-1} = 72$, these β values give

$$\beta_{101} + B\beta_{201} = 19 + 0.500 \times 107 = 73$$

IV. "Letagrop" calculations. The experimental data were also processed with the spectrophotometric version of the "Letagrop" program.¹² In Table 2 some experimental and calculated data are presented and in Table 3 a survey of the results of the calculations is given. U is the error squares sum, defined as $U = \sum(\varepsilon_{\text{calc}} - \varepsilon)^2$ and $\sigma(\varepsilon)$ the standard deviation in ε as defined in the program. The ε_{100} values (*cf.* Table 1), determined in nickel(II) perchlorate

solutions, were used in the "Letagrop" calculations.

In group II and III, Table 3, one complex at a time was included in the calculations. Since the best fit was obtained for the complexes with $(pqr) = (101)$ and (201) , these were included together. Efforts were made to determine β_{111} , β_{102} or β_{301} , together with β_{101} and β_{201} , by processing three complexes simultaneously. During the calculations, however, the third β value either became negative, or attained a small positive value with standard deviations of the same magnitude. It did not therefore seem likely that the three former complexes were present.

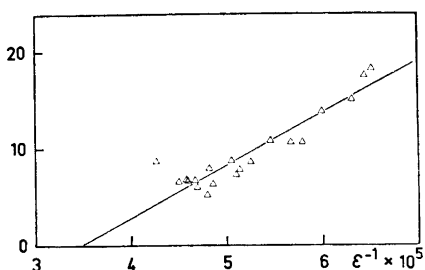


Fig. 9. The left-hand side of eqn. (6) as a function of ϵ^{-1} for $\lambda = 270$ nm, different A B values and $\text{pH} \sim 2$. $\beta_{201} = 107$ and $\epsilon_{201} = 25\,300$ are inserted. From the slope and intercept of the line $\beta_{101} = 19\text{ M}^{-1}$ and $\epsilon_{101} = 28\,100\text{ M}^{-1}\text{ cm}^{-1}$ are obtained.

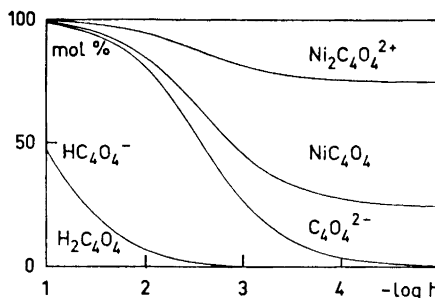


Fig. 10. The distribution of squaric acid as a function of $-\log h$ for the nickel squarate system when $B = 100.0$ mM.

As no complexes other than (101) and (201) could be detected, final calculations were performed. Solutions containing the highest percentage of the (101) complex were chosen and the β_{101} and ϵ_{101} values varied in the calculations while the β_{201} and ϵ_{201} values were kept constant. In this way the ϵ_{101} values could be determined with the highest possible accuracy. The ϵ_{201} values were determined in a similar manner. These ϵ_{101} and ϵ_{201} values (*cf.* Table 1) were then inserted in a final calculation, using data from all the solutions, the following values being obtained for the stability constants:

$$\begin{aligned} \beta_{101} &= (19.5 \pm 1.2)\text{M}^{-1}; & \log \beta_{101} &= 1.29 \pm 0.03 \\ \beta_{201} &= (106 \pm 4)\text{M}^{-2}; & \log \beta_{201} &= 2.03 \pm 0.02 \end{aligned}$$

EMF MEASUREMENTS

In order to confirm the results obtained by spectrophotometric methods, some potentiometric titrations were carried out. The distribution of complexes can be seen in Figs. 4, 10, 11, and 12. If a nickel solution is added to a sodium squarate solution, both solutions having $\text{pH} 3$, and if A is kept constant, the free hydrogen ion concentration increases. Owing to the slight solubility

of squarate complexes A is rather low and only small amounts of hydrogen ions will be liberated and thus only small changes in h can be detected if no precipitates are allowed to form.

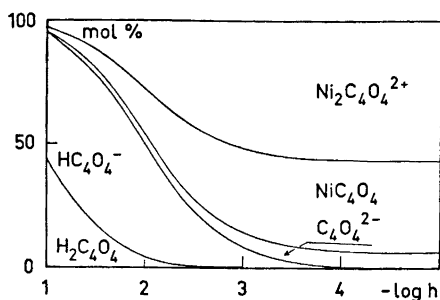


Fig. 11. The distribution of squaric acid as a function of $-\log h$ for $B=300.0$ mM.

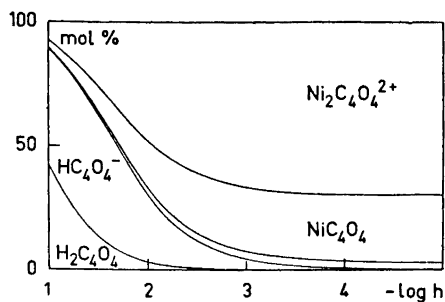


Fig. 12. The distribution of squaric acid as a function of $-\log h$ for $B=500.0$ mM.

In order to avoid the formation of precipitates without starting with too small an A value, sodium squarate solutions were diluted with nickel perchlorate solutions, *i.e.* A decreased with increasing B during the titrations (*cf.* Table 4). The hydrogen ion concentrations were measured by means of the cell described earlier.²

Table 4. Emf data. The concentrations of NiA and Ni_2A^{2+} have been calculated by means of the formulae $\beta_{101} a b$ and $\beta_{201} a b^2$, respectively. $\Delta_1 E$ is the "error" when the complexes with (pqr) (011), (021), (101) and (201) are included in the calculations and $\Delta_2 E$ the error based on (011) and (021) only. The β_{101} and β_{201} values obtained by spectrophotometric methods have been used.

A mM	B mM	NiA mM	Ni_2A^{2+} mM	$-\log h_{\text{calc}}$	$\frac{H - h_{\text{calc}}}{A}$	$\Delta_1 E$ mV	$\Delta_2 E$ mV
2.150	0	0	0	3.234	0.480	0.2	0.2
1.843	71.44	0.59	0.22	3.054	0.327	-0.2	-10.5
1.613	125.0	0.59	0.40	3.001	0.240	0.3	-13.0
1.433	166.7	0.53	0.48	2.985	0.188	0.1	-13.8
1.290	200.0	0.50	0.54	2.983	0.155	0.1	-13.8
1.075	250.0	0.37	0.51	2.992	0.116	0.2	-13.0
0.921	285.8	0.30	0.47	3.006	0.094	-0.1	-12.2
0.806	312.6	0.26	0.44	3.004	0.083	-0.1	-11.2
0.717	333.4	0.22	0.40	3.015	0.074	-0.1	-10.3

TREATMENT OF THE DATA

Data from the titrations are given in Table 4. Using the symbols v_0 , H_0 and A_0 for the volume and total concentrations of the original sodium squarate solution and v_t , H_t , and B_t for those of the nickel perchlorate solution added, then

$$H = \frac{v_0 H_0 + v_t H_t}{v_0 + v_t}; \quad A = \frac{v_0 A_0}{v_0 + v_t}; \quad B = \frac{v_t B_t}{v_0 + v_t}$$

The "Letagrop" program for potentiometric titrations¹³ was used to calculate $-\log h_{\text{calc}}$, H , $(H - h_{\text{calc}})/A$, and ΔE , where $\Delta E = E_{\text{calc}} - E$ was the "error" in the potential. The β values determined spectrophotometrically were inserted and not varied during the calculations.

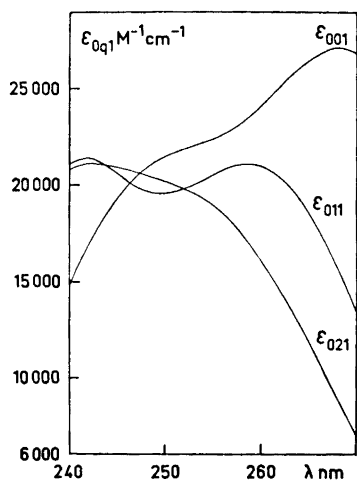


Fig. 13. ϵ_{0q1} as a function of λ . The ϵ_{0q1} values are calculated by the Letagrop program.

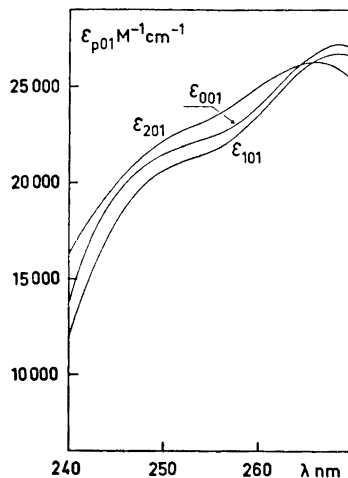


Fig. 14. ϵ_{p01} as a function of λ . The ϵ_{p01} values are calculated by the Letagrop program.

The $(-\log h)$ values decreased when the nickel perchlorate solution with $-\log h = 3.19$ was added, as long as the concentrations of the nickel squarate complexes increased. The "errors" $\Delta_1 E$ obtained when the two nickel complexes were included in the calculations, were small, whereas $\Delta_2 E$, obtained when these complexes were excluded, were significant. The emf measurements thus confirm the β values determined by spectrophotometric methods.

RESULTS AND DISCUSSION

The "best values" obtained from the spectrophotometric data are

$$\log \beta_{101} = 1.29 \pm 0.03$$

$$\log \beta_{201} = 2.03 \pm 0.02$$

where the errors given correspond to an error of 3σ in β . The corresponding ϵ values are shown in Table I.

These β values have been used together with the previously determined

$$\log \beta_{011} = 3.19$$

$$\log \beta_{021} = 4.15$$

to calculate the distribution of the squarate ion, A^{2-} , between the different complexes at some nickel concentrations (*cf.* Figs. 10, 11, and 12). From the diagrams it would seem most favourable to study the complex formation at pH 4–5. At this pH, however, most of the squaric acid, not bound to nickel, is present as the squarate ion, A^{2-} , with molar absorptivities very similar to those for NiA and Ni_2A^{2+} (*cf.* Table 1). Hence if spectrophotometric methods are used it is necessary to work at other pH values. At pH 2, for instance, A^{2-} , NiA , and Ni_2A^{2+} together represent 68 % of the total squaric acid concentration when $B = 0.5$ M and A^{2-} 6 % when $B = 0$.

The absence of complexes containing more than one squarate ion is not surprising considering the low total concentration of squarate ions, $A \leq 3$ mM compared to the total nickel ion concentration, $B \leq 600$ mM. The similarity of the absorptivities for the squarate ion and its metal complexes was also noticed by Tedesco and Walton.⁶ They found that the association of the squarate ion with copper(II) or iron(III) did not affect the ultra-violet absorption of the ion for $\lambda > 225$ nm. In their spectrophotometric measurements they used the absorption of the copper(II) and iron(III) complexes in the visible range of the spectrum. No such absorption occurs, however, for the nickel complexes. In their work on nickel(II) squarate complexes they used a paper chromatographic method and, assuming that only one complex, NiC_4O_4 , was formed they obtained the formation constant $\log \beta = 1.48$. This value agrees well with those determined in this work, *i.e.* $\log \beta_{101} = 1.29$ and $\log \beta_{201} = 2.03$, considering the differences in assumptions and ionic strength.

In more concentrated nickel squarate solutions precipitates are formed after some time. The formation of precipitates can be related to the concentration of the complex Ni_2A^{2+} and not to that of the complex NiA . Some solutions were prepared with constant $A = 5.07$ mM and $B = 300$ mM and varying perchlorate ion concentrations ranging from 600 to 1800 mM. These solutions thus had varying total molarity. Precipitates were only formed in the solutions with the highest perchlorate concentrations. It therefore seems probable that the precipitate contains the ions Ni_2A^{2+} and ClO_4^- . Analysis of the precipitate gave the following results: Found: C 8.8; H 2.7; Cl 12.6. Calc. for $Ni_2C_4O_4(ClO_4)_2 \cdot 7H_2O$: C 8.7; H 2.5; Cl 12.8.

The complex formation between nickel(II) and squarate ions is weaker than was expected, when the investigation was started. The rather small stability constants and the fact that the electronic spectrum of the squarate ion is only slightly affected by the complex formation show that the bonds between the central ion and the ligand involve rather weak σ - or electrostatic interactions. π -Bonding between the nickel d -orbitals and the empty antibonding orbitals of the aromatic system can be disregarded.

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