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

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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 NaClO<sub>4</sub>. 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 For all Details of the following equilibria and corresponding stability constants in the Ni<sup>2+</sup> - H<sup>+</sup> - C<sub>4</sub>O<sub>4</sub><sup>2-</sup> system: Ni<sup>2+</sup> + C<sub>4</sub>O<sub>4</sub><sup>2-</sup>  $\Rightarrow$  NiC<sub>4</sub>O<sub>4</sub> log  $\beta_{101} = 1.29 \pm 0.03$  2Ni<sup>2+</sup> + C<sub>4</sub>O<sub>4</sub><sup>2-</sup>  $\Rightarrow$  Ni<sub>2</sub>C<sub>4</sub>O<sub>4</sub><sup>2+</sup> log  $\beta_{201} = 2.03 \pm 0.02$ 

The errors given correspond to an error of  $3\sigma$  in  $\beta$ , where  $\sigma$  is the standard deviation in  $\beta$ .

Quaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, H<sub>2</sub>C<sub>4</sub>O<sub>4</sub>) was not known Uuntil 1959, when it was first synthetized by Cohan et al. 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.<sup>2</sup> Recently acidity constants have been reported by Gelb<sup>3</sup> (p $K_{\rm a1}$ =0.51) and by Schwartz and Howard<sup>4,5</sup> (p $K_{\rm a1}$ =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, who determined formation constants for iron(III), uranium(VI), aluminium(III), copper(II), manganase(II), cobalt(II), and nickel(II), and by Cilindro et al. 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 NaClO<sub>4</sub> as supporting electrolyte. The pH range was 3.5-4 and the temperature  $25^{\circ}$ 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. The EDTA solution was prepared from Titriplex 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.

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.<sup>2</sup>

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  $25.0 \pm 0.1$ °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. The sodium perchlorate concentration was then  $3.000 \, \text{M} - 2A - 2B - h$ .

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

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

 $egin{array}{lll} A & ext{total concentration of squaric acid, } H_2A \ a & ext{free concentration of squarate ions, } A^{2-} \ B & ext{total concentration of nickel ions, } Ni^{2+} \ \end{array}$ 

b free concentration of nickel ions,  $Ni^{2+}$ 

H total concentration of hydrogen ions, H<sup>+</sup>

h free concentration of hydrogen ions, H<sup>+</sup> free concentration of  $\text{Ni}_b \text{H}_q \text{A}_r$   $^{(2p+q-2r)+}$ 

A absorbance

optical pathlength

apparent molar absorptivity equilibrium constant for the reaction

$$p\mathrm{Ni}^{2+} + q\mathrm{H}^+ + r\mathrm{A}^{2-} \rightleftharpoons \mathrm{Ni}_{q}\mathrm{H}_{p}\mathrm{A}_{r}^{(2p+q-2r)+}$$

defined so that

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

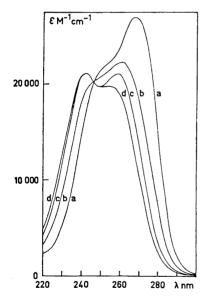
 $e_{pqr}$  molar absorptivity for the complex  $\text{Ni}_p H_q A^{(2p+q-2r)+}$  $v_0, A_0, H_0$  volume and total concentrations in the starting solution in the emf measurements

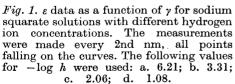
 $v_t, A_t, B_t, H_t$  volume and total concentrations in the solution added in the emf measurements

 $\boldsymbol{\mathit{E}}$ potential

### SPECTROPHOTOMETRIC MEASUREMENTS

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





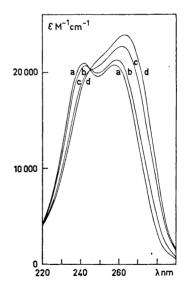
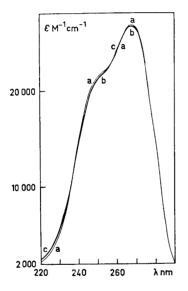


Fig. 2.  $\varepsilon$  data as a function of  $\lambda$  for solutions with A = 0.1201 mM and different nickel perchlorate concentrations. The following values for B and  $-\log h$  were used: a. 0 mM and 2.03; b. 85.18 mM and 2.00; c. 352.4 mM and 1.93; d. 598.6 mM and 1.86.

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 previously <sup>2</sup> the HA<sup>-</sup> anion dominates the squaric acid system at pH 2 while the A<sup>2-</sup> 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<sup>2-</sup>, or that complex formation is negligible.



100 mol %  $HC_{4}O_{4}^{-} C_{4}O_{4}^{2-}$   $O = \frac{1}{2} \frac{1}{3} \frac{1}{4} - \log h$ 

Fig. 3.  $\varepsilon$  data as a function of  $\lambda$  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:

$$A_{s} = \varepsilon l A = l \sum_{p} \sum_{q} \sum_{r} \varepsilon_{pqr} c_{pqr}$$
 (1)

Inserting the expression

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

in eqn. (1) gives

$$\varepsilon = \frac{\sum \sum \sum r \epsilon_{pqr} \beta_{pqr} b^p h^q a^r}{\sum \sum r \sum r \beta_{pqr} b^p h^q a^r}$$
(2)

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

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

The constants  $\beta_{011}$  and  $\beta_{021}$  have been determined earlier by means of emf methods at the same ionic strength, 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  $3\sigma$  in  $\beta$ . Using these values of the constants, the experimental data from solutions not containing nickel were processed with the spectrophotometric version of the "Letagrop" program. When  $\beta_{011}$  was varied together with  $\varepsilon_{001}$ ,  $\varepsilon_{011}$ , and  $\varepsilon_{021}$  for the 16 wavelengths,  $\log \beta_{011} = 3.13 \pm 0.05$  was obtained as "the best value". The  $\beta$  values calculated from the emf measurements were used in the following, since these are the most accurate values. The  $\varepsilon$  values calculated holding these  $\beta$  values constant are given in Table 1 and used in the following.

Table 1. Molar absorptivities,  $\varepsilon_{pqr}$ , in  $M^{-1}$  cm<sup>-1</sup> calculated with the Letagroup program. The errors are given as  $3\sigma$  where  $\sigma$  is the standard deviation in  $\varepsilon$ .

λnm	$\varepsilon_{021}$	$\varepsilon_{011}$	$arepsilon_{001}$	$\varepsilon_{101}$	$\varepsilon_{201}$	€ <sub>100</sub>
240	$20.800 \pm 470$	$21\ 100 \pm 120$	$14\ 800 \pm 140$	$13\ 100 \pm 560$	$16\ 300 \pm 310$	0.011
242	$21\ 100 \pm 440$	$21\ 400\pm120$	$16900 \pm 120$	$15\ 000\pm510$	$18\ 000 \pm 260$	0.011
244	$21\ 000 \pm 460$	$20\ 900 \pm 120$	$18600 \pm 130$	$17\ 100 \pm 330$	$19\ 400\pm 180$	0.011
246	$20\ 800 \pm 470$	$20\ 200\pm120$	$20\ 000 \pm 140$	$18600 \pm 310$	$20\ 600 \pm 160$	0.010
248	$20\ 500 + 450$	19700 + 120	$20\ 900 \pm 130$	$19\ 900 \pm 360$	$21\ 500 \pm 200$	0.010
250	$20\ 200 + 440$	$19\ 600 \pm 110$	$21\ 500 \pm 130$	$20\ 600\pm310$	$22\ 200 \pm 210$	0.010
252	$19\ 900 \pm 380$	$19.800 \pm 100$	$21\ 900 \pm 110$	$21\ 100 \pm 320$	$22\ 700 \pm 210$	0.009
254	$19\ 300 \pm 380$	$20\ 300 + 100$	$22\ 200 + 110$	$21\ 400 + 300$	$23\ 100\pm210$	0.009
256	18600 + 390	$20\ 800 \pm 100$	$22\ 600 \pm 110$	$21\ 900 \pm 350$	$23\ 600\pm230$	0.009
258	$17\ 500 + 420$	$21\ 100 \pm 110$	$23\ 200 + 120$	$22\ 600 + 370$	$24\ 300 + 240$	0.009
260	$16\ 100 + 450$	$21\ 000 \pm 120$	$24\ 100 + 130$	$23\ 600 + 400$	$25\ 000 \pm 260$	0.009
262	14600 + 540	$20\ 400 + 140$	$25\ 100+160$	24700 + 470	$25\ 600 + 300$	0.009
264	12800 + 650	$19\ 300 + 170$	$26\ 100 + 190$	$25\ 700 \pm 500$	$26\ 100 \pm 370$	0.009
266	$10900 \pm 760$	17700 + 200	$26\ 800 \pm 220$	$26\ 400 + 490$	$26\ 300 \pm 370$	0.008
268	$9\ 000 + 940$	$15600 \pm 250$	$27\ 200 + 270$	$26700 \pm 510$	$26\ 000 \pm 360$	0.008
270	7000 + 1080	$13\ 400 + 280$	$26\ 900 + 320$	$26\ 500 + 450$	$25\ 300 + 400$	0.007

II. q=1. In eqn. (1)  $\mathrm{Ni}_p\mathrm{H}_q\mathrm{A}_r^{(2p+q-2r)+}$  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,  $A \le 3$  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

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

or

$$[\varepsilon(1+\beta_{011}h+\beta_{021}h^2)-(\varepsilon_{001}+\varepsilon_{011}\beta_{011}h+\varepsilon_{021}\beta_{021}h^2)]/\varepsilon b = = -\sum_{p}b^{p-1}(\beta_{p11}h+\beta_{p01})+\sum_{p}b^{p-1}(\varepsilon_{p11}\beta_{p11}h+\varepsilon_{p01}\beta_{p01})\varepsilon^{-1}$$
(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  $B \gg \text{A}$ , 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  $\varepsilon^{-1}$ ,  $\sum_{p} B^{p-1} \varepsilon_{p11} \beta_{p11}$ , is constant. The left-hand side

of the equation was plotted against  $\varepsilon^{-1}$ , (cf. Fig. 5) to test whether or not there was a linear correlation. It was obvious that there was no linear correlation Ni<sub>2</sub>HA<sup>(2p-1)+</sup> thus not being the main complexes formed.

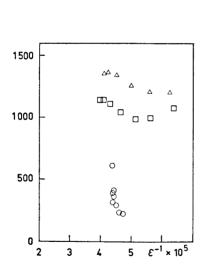


Fig. 5. The left-hand side of eqn. (5) divided by h, as a function of  $\varepsilon^{-1}$  for different wavelengths. A=1.157 mM, B=500.0 mM and the values for  $\lambda$  are  $\bigcirc$  254 nm,  $\square$  268 nm and  $\triangle$  270 nm.

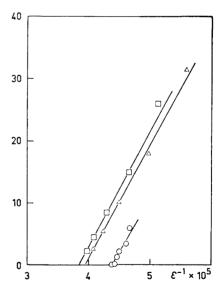


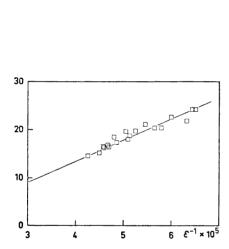
Fig. 6. The left-hand side of eqn. (5) as a function of  $\varepsilon^{-1}$  for different wavelengths. A=1.157 mM, B=500.0 mM and  $1.3 \le -\log h \le 3.7$ . The  $\lambda$  values are  $\bigcirc$  254 nm,  $\bigcirc$  268 nm and  $\triangle$  270 nm. From the slope and intercept for  $\lambda=270$  nm  $\sum_{p}\beta_{p01}b^{p-1}=72$  M<sup>-1</sup> and  $\varepsilon_{101}=25$  300 M<sup>-1</sup> cm<sup>-1</sup> are

III. q=0. The complexes  $\mathrm{Ni}_p\mathrm{HA}^{(2p-1)+}$  were then neglected and the complexes  $\mathrm{Ni}_p\mathrm{A}^{(2p-2)+}$  tested by inserting the same data in eqn. (5) (cf. Fig. 6). This time a linear correlation was obtained. The complexes  $\mathrm{Ni}_p\mathrm{A}^{(2p-2)+}$  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,  $\varepsilon_{001}$ . Supposing all  $\varepsilon_{p01} \approx \varepsilon_{101}$ , the slope and intercept of the line give

$$\sum_{p} \beta_{p01} B^{p-1} = 72; \ \varepsilon_{101} = 25 \ 300$$

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  $\varepsilon^{-1}$ . If NiA is supposed to be the only nickel complex present, the slope and intercept of the line give



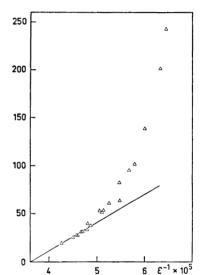


Fig. 7. The left-hand side of eqn. (5) as a function of  $\varepsilon^{-1}$  for  $\lambda = 270$  nm, different A and B values and pH ~ 2. From the slope and intercept  $\beta_{101} = 4$  M<sup>-1</sup> and  $\varepsilon_{101} = 108\ 000$  M<sup>-1</sup> cm<sup>-1</sup> are obtained.

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

$$\beta_{101} = 4$$
;  $\varepsilon_{101} = 108 000$ 

The  $\varepsilon_{101}$  value obtained seemed to be too high compared to  $\varepsilon_{001} = 26$  900. To test whether or not the complex Ni<sub>2</sub>A<sup>2+</sup> 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  $\varepsilon^{-1}$  (cf. Fig. 8). If all nickel complexes except Ni<sub>2</sub>A<sup>2+</sup> were neglected and data from solutions with the highest B values (and thus the highest  $\varepsilon$  values) were used, then

Table 2. Spectrophotometric data for 14 solutions. The values given are  $\log h$ , A and B for each solution, followed by  $\varepsilon$ ,  $\varepsilon_{\rm calc}$ , and  $\varepsilon_{\rm calc} - \varepsilon$  for the 16 wavelengths. The concentrations are expressed in M and the molar absorptivities in  ${\rm M}^{-1}$  cm<sup>-1</sup>, all absorptivities are multiplied by a factor  $10^{-1}$ .

-2.006359	0.000120 2001.513	0.085180	2064.000			2061.000	2053.878	
2010.000	2001-513	-8.487 -4.237	1995-000	2055-626	-8.373	1993.000	20554878	-7.121
2023.000	2018.762	4.696	2057.000	1995-149	0.149 4.246	2096.000	1997.508 2101.508	4.508 5.508
2125.000	2128.220	3.220	2127.000	2061.246 2127.914	0.914	2091.000	2087.901	-3.099
2009.000	2002.890	-6.110	1886.000	1876.455	-9.545	1724.000	1709-944	-14.056
1534.000	1518.044	-15.955			,,,,,	2.2.000		210030
-1.577655	0.000120	0.200400						
1927.000	1914.278	-12.722	2004.000	1992.687	-11.313	2027.000	2024-615	-2.385
2019.000	2023.357	4.357	2012.000	2024.872	12.872	2022.000	2041.216	19.216
2052.000	2069.748	17.748	2090.000	2108.779	18.779	2131.000	2150.328	19.328
2167.000	2184.606	17.606	2184.000	2200.076	16.077	2172.000	2184.211	12.211
2120.000	2130.231	10.231	2025.000	2036.253	11.253	1892.000	1901-754	9.754
1727.000	1736.506	9.506						
~1.937099	0.000120	0.352400	10// 000		4 405	2002 000	2005 017	
1846.000	1838.382	-7.618	1946-000	1941.315	-4.685	2002.000	2005.917	3.917
2029.000 2106.000	2038.667 2127.829	9.667 21.829	2047.000 2146.000	2065.158 2167.909	18.158 21.909	2072.000 2189.000	2095.802 2211.139	23.802 22.139
2230.000	2253.098	23.098	2259.000	2283.868	24.869	2271.000	2291.619	20.619
2251.000	2268.308	17.308	2195.000	2206.470	11.470	2090.000	2103.388	13.388
1548.000	1563.847	15-847			•••	•••••		******
-1.908400	0.000120	0.462100						
1618.000	1806.648	-11.352	1927.000	1921.815	-5.184	1998.000	2002.263	4.263
2042.000	2051.729	9.729	2075.000	2090.542	15.542	2109.000	2128.380	19.380
2146.000	2162.013	16.013	2186.000	2202.814	16.814	2228.000	2247.021	19.021
2273.000	2292.837	19.637	2310.000	2331.036	21.036	2329.000	2350.318	21.318
2320.000	2342-089	22.089	2276.000	2295.893	19.893	2192.000	2208.179	16.179
2054.000	2080.873	24.873						
-1.888100	0.000120	0.541400 5.965	1004 000	1012 424		1987.000	2002 024	15.825
1786.000 2045.000	1791.965 2061.301	16.301	1904.000 2086.000	1913.836 2106.822	9.837 20.822	2126.000	2002.824 2148.621	22.621
2165.000	2183.019	18.019	2207.000	2224.275	17.275	2246.000	2269.059	23.059
2291.000	2316.995	25.995	2334.000	2359.200	25.200	2360.000	2384.720	24.720
2360.000	2384.687	24.687	2325.000	2346. 867	21.868	2251.000	2267.480	16.480
2130.000	2146.621	16.621		25.0000				
-1.871200	0.000120	0.598600						
1773.000	1785.295	12.296	1897.000	1910.945	13.945	1987.000	2004.688	17.688
2052.000	2068.163	16.163	2100.000	2117.454	17.454 17.750	2143.000	2161.494	18.494
2182.000	2196.228	14.228	2220.000	2237.750	17.750	2262.000	2282.850	20.850
2310.000	2331.551	21.951	2355.000	2376.353	21.353	2385.000	2405.326	20.327
2390.000	2409.865	19.865	2360.000	2376.638	16.638	2292.000	2301.898	9.898
2179.000	2184.529	5.529						
-4.973000	0.001000	0.0						
1477.000	1490.305 2000.327	13.305 10.327	1688.000 2082.000	1698.283 2090.958	10.284 8.959	1862.000 2143.000	1866.789 2150.799	4.789 7.799
2180-000	2189-603	9.603	2211.000	2220.864	9.864	2250.000	2261-027	11.027
2310.000	2320.537	10.537	2392.000	2401.067	9.067	2491.000	2501.405	10.405
2585.000	2598.861	13.861	2653.000	2669.023	16.023	2679-000	2698-136	19.136
2657.000	2672.805	15.805						
-4.948999	0.001000	0.075000						
1428.000	1433.390	5.391	1591.000	1625.018	34.018	1802.000	1805.594	3.594
1933.000	1948.490	15.490	2037.000	2053.266	16.266	2111.000	2123.266	12.266
2155.000	2167.078	12.078	2190.000	2203.135	13.135	2231.000	2247-674	16.674
2298.000	2313.771	15.771	2386.000	2401.393	15.393	2485.000	2499.301	14.301
2578.000	2589.467	11.467	2641.000	2649.609	8.609	2661.000	2666.507	5.508
2630.000 -4.757999	2632.617	2.817						
1435.000	1443.375	8.375	1627.000	1631.480	4.480	1801.000	1809.844	8.844
1944-000	1951.833	7.833	2048-000	2056.284	8.285	2120.000	2126.832	6.832
2165.000	2171.412	6.412	2202.000	2208.619	6.619	2245.000	2253.965	8.965
2314.000	2320.336	6.336	2401.000	2406.990	5.990	2506.000	2502.103	-3.894
2595.000	2588.605	-6.395	2656.000	2644.988	-11.012	2674.000	2657.325	-16.675
2641-000	2615.813	-21.187						•••••
-2.711300	0.001157	0.500000						
1563.000	1592.073	29.073	1732.000	1753.831	21.831	1884.000	1896.000	12.001
2007-000	2013.313	6.313	2102.000	2098.282	~3.717	2166.000	2162.509	-3.491
2212.000	2208.750	-3.250	2253.000	2252.319	-0.681	2302.000	2301.344	-0.656
2363.000	2363.726	0.726	2431.000	2433.394	2.394	2493.000	2499.833	6.833
-1.000	-1.000	0.0	-1.000	-1.000	0.0	2518.000	2545.053	27.054
2453.000 -2.400259	2472.620 0.001157	19.620						
1628-000	1632.189	4.189	1783.000	1783.525	0.526	1913.000	1911.684	-1.316
2017-000	2014.389	-2.611	2095.000	2088.930	-6.070	2152.000	2147.378	-4.622
2198.000	2191.875	-6.125	2240.000	2235.325	-4.675	2288.000	2283.915	-4.085
2345.000	2343.264	-1.736	2404.000	2406.472	2.472 27.197	2455.000	2462-808	7.808
2484.000	2501.152	17.152	2481.000	2508.197	27.197	2444.000	2467.195	23.195
2365.000	2383.060	18.060						
-2.117999	0.001157	0.500000						
1724.000	1692.787	-31.213	1861.000	1828.344	-32.656	1957.000	1935.475	-21.525
2034-000	2016.330	-17.670	2092.000	2075.207	-16.793 -13.963	2141.000	2124.790	-16.210
2180.000	2166.314	-13.686	2223.000	2209.037	-13.963	2269.000	2256.242	-12.757
2319.000 2411.000	2310-222	-8.777 10.617	2367.000	2362.944	-4.056 17.035	2401.000	2403.422 2345.527	2.422 15.527
2225.000	2421.616 2243.851	18.851	2370.000	24014033	11.0032	2330.000	2343.327	120221
-1.845155	0.001157	0.500000						
1807-000	1775.016	-31.984	1911.000	1889.073	-21.927	1977.000	1968.004	-8.996
2021-000	2019.746	-1.254	2056-000	2057.583	1.583	2091-000	2094.801	3.801
2128.000	2131.456	3.456	2169.000	2171.847	2.847	2214.000	2215.382	1.382
2257.000	2260.134	3.134	2290.000	2296.830	6.830	2302.000	2314.320	12.320
2285.000	2304.240	15.240	2239.000	2259.716	20.716	2144.000	2170.429	26.429
2007-000	2045.278	38.278						
-1.584200	0.001157	0.500000						
1914-000	1671-577	-42.423	1989.000	1960.196	-28.804	2024-000	2006.737	-17-262
2036.000	2025-455	-10.545 -2.844	2047.000 2140.000	2039.055 2124.890	-7.945 -15.110	2069.000	2061.030	-7.970 -19.773
2093-000 2212-000	2090.156 2189.930	-2.844 -22.070	2140.000	2124.890	-15.110 -22.085	2180.000 2214.000	2160.227 2191.219	-22.781
	4 TO3. 230	-224010	2080.000	2064.940	-15.060	1948.000	1943-136	-4.863
	2145-910							
2168.000 1750.000	2145.918 1791.134	-22.082 1.134	2080.000	20018 740	-13.000	1748.000	17436130	-4.003

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

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

$$\beta_{201} = 107$$
;  $\varepsilon_{201} = 27600$ 

were obtained.

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

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

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

were inserted. The  $\varepsilon_{201}$  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  $\beta$  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. 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  $U = \sum (\varepsilon_{\rm calc} - \varepsilon)^2$  and  $\sigma(\varepsilon)$  the standard deviation in  $\varepsilon$  as defined in the program. The  $\varepsilon_{100}$  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  $\beta_{111}$ ,  $\beta_{102}$  or  $\beta_{301}$ , together with  $\beta_{101}$  and  $\beta_{201}$ , by processing three complexes simultaneously. During the calculations, however, the third  $\beta$  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.

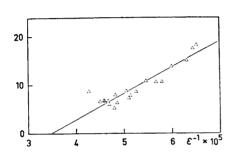


Fig. 9. The left-hand side of eqn. (6) as a function of  $\varepsilon^{-1}$  for  $\lambda = 270$  nm, different A B values and pH  $\sim 2$ .  $\beta_{201} = 107$  and  $\varepsilon_{201} = 25\,300$  are inserted. From the slope and intercept of the line  $\beta_{101} = 19\,\mathrm{M}^{-1}$  and  $\varepsilon_{101}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

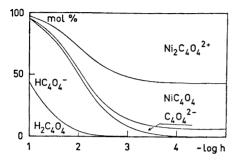
As no complexes other than (101) and (201) could be detected, final calculations were performed. Solutions containing the highest percentage of the (101) complex were chosen and the  $\beta_{101}$  and  $\varepsilon_{101}$  values varied in the calculations while the  $\beta_{201}$  and  $\varepsilon_{201}$  values were kept constant. In this way the  $\varepsilon_{101}$  values could be determined with the highest possible accuracy. The  $\varepsilon_{201}$  values were determined in a similar manner. These  $\varepsilon_{101}$  and  $\varepsilon_{201}$  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:

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

### 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 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.



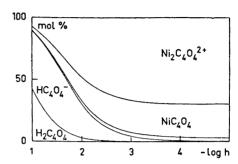


Fig. 11. The distribution of squaric acid as a function of  $-\log h$  for B = 300.0 mM.

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.<sup>2</sup>

Table 4. Emf data. The concentrations of NiA and Ni<sub>2</sub>A<sup>2+</sup> have been calculated by means of the formulae  $\beta_{101}$  a b and  $\beta_{201}$  a b<sup>2</sup>, 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  $\beta_{101}$  and  $\beta_{201}$  values obtained by spectrophotometric methods have been used.

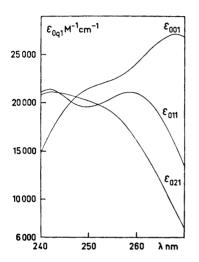
A mM	$B~\mathrm{mM}$	NiA mM	Ni <sub>2</sub> A <sup>2+</sup> mM	$-\log h_{\mathrm{calc}}$	$\frac{H - h_{\text{calc}}}{A}$	$\Delta_1 E \text{ mV}$	$\it \Delta_2 E \; { m mV}$
2.150	0	0	0	3.234	0.480	0.2	0.2
1.843	71.44	0.59	0.22	3.054	0.327	-0.2	-10.5
1.613	125.0	0.59	0.40	3.001	0.240	0.3	-13.0
1.433	166.7	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

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

The "Letagrop" program for potentiometric titrations <sup>13</sup> was used to calculate  $-\log h_{\rm calc}$ , H,  $(H-h_{\rm calc})/A$ , and  $\Delta E$ , where  $\Delta E=E_{\rm calc}-E$  was the "error" in the potential. The  $\beta$  values determined spectrophotometrically were inserted and not varied during the calculations.



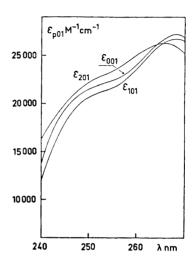


Fig. 13.  $\varepsilon_{0q1}$  as a function of  $\lambda$ . The  $\varepsilon_{0q1}$  values are calculated by the Letagrop program.

Fig. 14.  $\varepsilon_{po1}$  as a function of  $\lambda$ . The  $\varepsilon_{po1}$  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  $\beta$  values determined by spectrophotometric methods.

## RESULTS AND DISCUSSION

The "best values" obtained from the spectrophotometric data are

$$\begin{array}{ll} \log & \beta_{101} = 1.29 \pm 0.03 \\ \log & \beta_{201} = 2.03 \pm 0.02 \end{array}$$

where the errors given correspond to an error of  $3\sigma$  in  $\beta$ . The corresponding  $\varepsilon$  values are shown in Table 1.

These  $\beta$  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<sub>2</sub>A<sup>2+</sup> (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<sub>2</sub>A<sup>2+</sup> 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.<sup>6</sup> 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<sub>4</sub>O<sub>4</sub>, 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  $\mathrm{Ni_2A^{2^+}}$  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  $\mathrm{Ni_2A^{2^+}}$  and  $\mathrm{ClO_4^-}$ . Analysis of the precipitate gave the following results: Found: C 8.8; H 2.7; Cl 12.6. Calc. for  $\mathrm{Ni_2C_4O_4(ClO_4)_2}$  7H<sub>2</sub>O: 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  $\sigma$ - or electrostatic interactions.  $\pi$ -Bonding between the nickel d-orbitals and the empty antibonding orbitals of the aromatic system can be disregarded.

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### REFERENCES

- Cohan, S., Lacher, J. R. and Park, J. D. J. Am. Chem. Soc. 81 (1959) 3480.
   Alexandersson, D. and Vannerberg, N. G. Acta Chem. Scand. 26 (1972) 1909.
- 3. Gelb, R. I. Anal. Chem. 43 (1971) 1110.

- Gelb, R. I. Anal. Chem. 43 (1971) 1110.
   Schwartz, L. M. and Howard, L. O. J. Phys. Chem. 74 (1970) 4374.
   Schwartz, L. M. and Howard, L. O. J. Phys. Chem. 75 (1971) 1798.
   Tedesco, P. H. and Walton, H. F. Inorg. Chem. 8 (1969) 932.
   Cilindro, L. G., Stadlbauer, E. and Keller, C. J. Inorg. Nucl. Chem. 34 (1972) 2577.
   Vogel, A. I. Quantitative Inorganic Analysis, Longmans 1961, p. 435.
   Vogel, A. I. Quantitative Inorganic Analysis, Longmans 1961, p. 432.
   Gran, G. Analyst 77 (1952) 661.
   Burkov, K. A., Lilic, L. S. and Sillén, L. G. Acta Chem. Scand. 19 (1965) 14.
   Sillén L. G. and Warnqvist, B. Arkiv Kemi 31 (1969) 377.
   Brauner, P., Sillén, L. G. and Whiteker, R. Arkiv Kemi 31 (1969) 365.

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