

## Metal Ammine Formation in Solution. XXII. The Nickel(II) Triethanolamine System

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The present paper reports a potentiometric and spectrophotometric study of the nickel(II)–triethanolamine system. The formation curves ( $\bar{n}$ ,  $p[L]$ ) at different triethanolammonium concentrations are analyzed and constants determined for the formation of  $Ni(tea)^{2+}$ ,  $Ni_2(tea)_2^{2+}$  and of a hydrolysis product shown to be  $Ni_2(tea)_2(OH)_2^{2+}$  [ $tea = N(C_2H_4OH)_3$ ]. In 2 M  $teaHClO_4$  hydrolysis is suppressed and the first two consecutive formation constants for pure amine complex formation determined at 25 °C to be:  $K_1 = 10^{3.42 \pm 0.02} \text{ l mol}^{-1}$  and  $K_2 = 10^{0.87 \pm 0.03} \text{ l mol}^{-1}$ . In 0.5 M  $(teaH, Na)ClO_4$  values of  $K_1 = 10^{2.85 \pm 0.01} \text{ l mol}^{-1}$  and  $K_2 = 10^{0.14 \pm 0.03} \text{ l mol}^{-1}$  were determined. The hydrolysis constant  $\beta_{2,2}^* = [Ni_2(tea)_2(OH)_2^{2+}][H^+]^2 / [Ni(tea)^{2+}]^2$  was estimated to have the value  $10^{-14.8 \pm 0.4} \text{ mol l}^{-1}$ . The absorption curves in the visible region were analyzed, and spectra for  $Ni(tea)^{2+}$ ,  $Ni_2(tea)_2^{2+}$  and “ $Ni_2tea_2(OH)_2^{2+}$ ” were obtained.

Complex formation between triethanolamine and nickel(II) ions in solution has been studied by several authors.<sup>1–4</sup> Calorimetric and pH-measurements have been made by Sychow *et al.*<sup>1</sup> and pH-titrations and spectrophotometric measurements by Bhat *et al.*<sup>3</sup> Both of these authors demonstrated the existence of  $Ni(tea)^{2+}$  and  $Ni_2(tea)_2^{2+}$  and determined values for their formation constants, but only Bhat *et al.*<sup>3</sup> mention the disturbance caused by the presence of polynuclear hydroxo complexes. Cadiot-Smith<sup>4</sup> studied the system by base titrations and reports the successive formation of  $Ni(tea)^{2+}$ ,  $Ni_2(tea)_2(OH)_2^{2+}$  and

$Ni_4(tea)_4(OH)_6^{2-}$  by increasing pH. The formation of polymeric hydroxo complexes explain the fact that the authors concerned<sup>1,3</sup> obtain values for the second formation constant which are too high. Sklenskaya *et al.*<sup>2</sup> claim to have demonstrated the existence of  $Ni_3(tea)_3^{2+}$ , but their experimental results are undoubtedly attributable to the formation of hydroxo complexes. Triethanolamine nickel(II) salts of the composition  $Ni(tea)_2X_2$  have been prepared<sup>5</sup> and Rasmussen and coworkers<sup>6</sup> have determined the crystal structure of  $Ni(tea)_2(NO_3)_2$ . It was found to have an octahedral configuration in which each of the triethanolamine ligands is tridentate and facially coordinated by the nitrogen atom and two of the oxygen atoms. The oxygen atom on the third branch of the ligand is, as expected, not coordinated to nickel.

The present paper supplements the literature data with improved values for the formation constants  $K_1$  and  $K_2$  and with an estimated value for the hydrolysis constant of  $Ni(tea)^{2+}$ . Furthermore, the absorption spectra of the complexes and of the hydrolysis product have been estimated.

### EXPERIMENTAL

*Reagents and solutions.* All reagents were of analytical grade. The triethanolamine (tea) used was Merck *pro analysi* containing less than 1% diethanolamine. The various solutions were prepared in volumetric flasks by weighing or pipetting from stock solutions. A 2.50 M stock solution of  $teaHClO_4$  was prepared by neutralizing 5.00 M  $HClO_4$  with the pure amine and diluting to the double volume. Complete equivalence between amine and perchloric acid was ensured as described earlier.<sup>7</sup>

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Table 1. Glass electrode measurements on nickel(II)triethanolamine solutions in 2 M teaHClO<sub>4</sub> at 25 °C. pH + p[tea] = 8.12 ± 0.01.<sup>8</sup> Estimation of log K<sub>1</sub> and log K<sub>2</sub>.

No.	C <sub>Ni</sub>	C <sub>tea</sub>	p[tea]	pH	$\bar{n}$	log K <sub>1</sub> <sup>a</sup>	log K <sub>2</sub> <sup>a</sup>
1	0.02085	0.00663	3.743	4.377	0.311	3.397	
2	0.02092	0.01046	3.442	4.678	0.484	3.415	
3	0.02094	0.01625	3.026	5.094	0.731	3.460	
6 <sup>c</sup>	0.06291	0.1187	1.395	6.725	1.246		0.909
9 <sup>d</sup>	0.06274	0.1597	1.123	6.997	1.344		0.843
						Av. 3.42 ± 0.03 <sup>a</sup>	0.87 ± 0.03 <sup>b</sup>

<sup>a</sup>  $K_1 \cong \bar{n}/\{(1-\bar{n})[\text{tea}]\}$ . Mean of solutions 1–3. <sup>b</sup>  $K_2 \cong (\bar{n}-1)/\{(2-\bar{n})[\text{tea}]\}$ . Mean of 5 solutions with 1.2 ≤  $\bar{n}$  ≤ 1.4. <sup>c</sup> Calc.  $\alpha_0 = 0.0072$ ,  $\alpha_1 = 0.765$ ,  $\alpha_2 = 0.228$ . <sup>d</sup> Calc.  $\alpha_0 = 0.00322$ ,  $\alpha_1 = 0.640$ ,  $\alpha_2 = 0.357$ .

The stock solution of nickel(II)perchlorate (0.523 mol/l) and 0.476 mol/kg) was analyzed by electrolytic deposition of nickel in ammoniacal solution. pH was adjusted to ~5.8.

Spectrophotometric measurements (UV and Vis) were made with a Cary 118 spectrophotometer at room temperature (22–23 °C). Cells of pathlength 0.1 to 2 cm were used, the reference cells being filled with a corresponding nickel-free solution.

pH = -log[H<sup>+</sup>] was determined by glass electrode measurements at 25 °C as described previously.<sup>8</sup>

*Estimation of stability constants.* Table 1 shows some data for the complex formation between Ni(II) ions and triethanolamine (tea) in 2 M tea-

HClO<sub>4</sub> at 25 °C. C<sub>x</sub> denotes stoichiometric concentrations and [X] the molar concentrations of the individual species. p[tea] and pH were calculated using the previously determined value<sup>8</sup> for K<sub>teaH<sup>+</sup></sub> and the ligand number was calculated from the relationship (1), where [tea]' = [tea] + [H<sup>+</sup>] - [OH<sup>-</sup>]. As a consequence on the steric hindrance to the uptake of the second amine molecule,

$$\bar{n} = (C_{\text{tea}} - [\text{tea}'])/C_{\text{Ni}} \quad (1)$$

$$K_1 = [\text{Nitea}^{2+}]/([\text{Ni}^{2+}][\text{tea}]) \quad (2)$$

$$K_2 = [\text{Ni}(\text{tea})_2^{2+}]/([\text{Nitea}^{2+}][\text{tea}]) \quad (3)$$

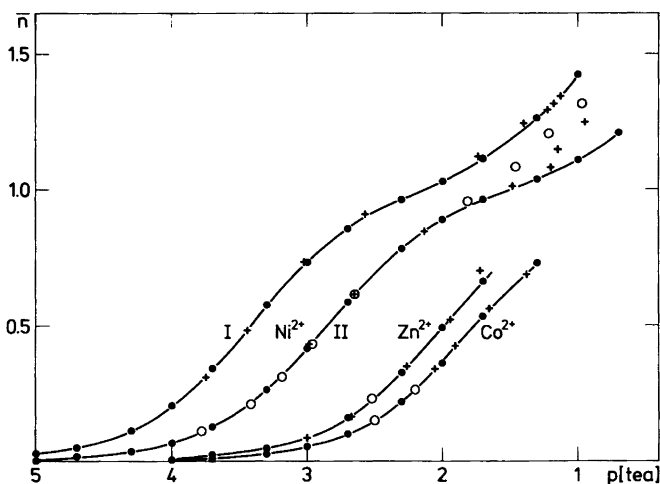


Fig. 1. Formation curves  $\bar{n}$  versus p[tea]. Curve I for nickel(II) in solutions with C<sub>tea<sup>+</sup></sub> = 2.00 M (+, exp; ●, calc); curve II for nickel(II) with C<sub>teaH<sup>+</sup></sub> = 0.50 M (+) and with C<sub>teaH<sup>+</sup></sub> ≅ 0.10 M, C<sub>Na<sup>+</sup></sub> = 0.40 M (○). The full curves are calculated by use of the estimated constants for pure amine complex formation neglecting hydrolysis. For comparison purposes the formation curves for zinc(II) and cobalt(II) in 0.5 M (teaH,K)NO<sub>3</sub> C<sub>tea<sup>+</sup></sub> = 0.40 M (+), C<sub>teaH<sup>+</sup></sub> = 0.10 M (○) drawn on the basis of earlier measurements<sup>14,15</sup> are shown.

Table 2a. Glass electrode measurements on nickel(II) triethanolamine solutions at 25 °C.  $C_{\text{teaHClO}_4} + C_{\text{NaClO}_4} = 0.50$  M.  $pK_{\text{teaH}^+} = 7.90 \pm 0.01$ .<sup>b</sup>

No.	$C_{\text{teaH}^+}$	$C_{\text{Ni}}$	$C_{\text{tea}}$	p[tea]	pH	$\bar{n}$	log $K_1$	log "K <sub>2</sub> " <sup>a</sup>
13	0.100	0.02094	0.01005	2.964	6.039	0.428	2.838	
14	0.500	0.02093	0.01000	2.980	5.283	0.428	2.853	
21	0.500	0.02097	0.08591	1.199	7.064	1.081		0.144
23	0.500	0.06280	0.1908	0.949	7.314	1.247		0.465
25	0.100	0.02095	0.08593	1.217	7.786	1.206		0.631
26 <sup>b</sup>	0.115	0.06285	0.1906	0.971	7.972	1.329		0.661
27 <sup>b</sup>	0.080	0.06267	0.2002	0.986	8.114	1.546		1.061
Mean of 8 solutions with $0.1 \lesssim \bar{n} \lesssim 0.8$						Av. $2.85 \pm 0.01$		

<sup>a</sup>  $K_2'' = (\bar{n} - 1) / \{ (2 - \bar{n}) [\text{tea}] \}$ . <sup>b</sup> Calc. with  $C_{\text{teaH}^+} = C_{\text{teaH}^+}^\circ + C_{\text{Ni}}''$ .

Table 2b. Calculation of hydrolysis constants with log  $K_1 = 2.85$  and log  $K_2 = 0.144$ .

No.	[tea]	$[\text{Ni}^{2+}]$	$[\text{Ni}(\text{tea})_2^{2+}]$	$[\text{Ni}(\text{tea})_2^{2+}]$	$C_{\text{Ni}}''$	$p\beta_{1,1}^*$	$p\beta_{2,2}^*$	$p\beta_{4,4}^*$
21	0.06324	0.000419	0.01843	0.001632	0.000488	8.64	14.27	25.23
23	0.1125	0.000582	0.04614	0.00726	0.00882	8.03	14.31	26.57
25	0.06067	0.0003715	0.01590	0.001351	0.00333	8.46	14.75	27.03
26	0.1070	0.000545	0.0411	0.00616	0.0150	8.41	15.29	28.76
27 <sup>a</sup>	0.1033	0.000388	0.02826	0.00408	0.0299	8.09	14.95	28.39
Mean of 9 solutions with $0.0003 < C_{\text{Ni}}'' < 0.03$ .						Av. $8.49 \pm 0.16$ 14.63 $\pm$ 0.34 26.63 $\pm$ 1.27		

<sup>a</sup> Solution 27 deposited a blue crystalline precipitate after a few hours.

$K_1$  and  $K_2$  can be calculated independently of each other as shown in the table; eqns. (2) and (3). The calculated values of both  $K_1$  ( $= 10^{3.42}$ ) and  $K_2$  ( $= 10^{0.87}$ ) are seen to be relatively good constants. Similar calculations are given in Table 2a for solutions with lower concentrations of  $\text{teaH}^+$ , in which  $C_{\text{teaHClO}_4} + C_{\text{NaClO}_4} = 0.5$  M. The value obtained for  $K_1$  ( $= 10^{2.85}$ ) in this medium is well-defined although lower than for 2 M  $\text{teaHClO}_4$ . However, the values for  $K_2 = (\bar{n} - 1) / \{ (2 - \bar{n}) [\text{tea}] \}$  show no constancy, and the drift in "K<sub>2</sub>" is due to hydrolysis. The influence of this drift can also be seen in Fig. 1, in which the formation curves for 2 M  $\text{teaHClO}_4$  (curve I) and for the 0.5 M salt medium (curve II) are plotted on the basis of data for all the measured solutions (Nos. 1–27). The full curves are calculated with the estimated constants. A tentative value for  $K_2$  in the 0.5 M medium of  $10^{0.144}$  (obtained for the solution with the lowest pH (No. 21 in Table 2a) was used. For curve I the calculated curve fits the experimental points up to the highest measured  $\bar{n}$ -values. The same is not the case for curve II for  $\bar{n} \geq 1$ , and the deviations from the calculated curve are as expected especially pronounced

for the ○-points corresponding to the lowest triethanolammonium concentrations. The midpoint relationship  $\log(K_1 K_2) = 2p[\text{tea}]_{\bar{n}=1}^-$  is found to be valid for curve I where  $\log(K_1 K_2) = 3.42 + 0.87 = 4.29$  and  $p[\text{tea}]_{\bar{n}=1}$  is read from the curve to be 2.13. Applied to curve II with  $p[\text{tea}]_{\bar{n}=1} = 1.50$  we obtained for  $\log K_2$ :  $2 \times 1.50 - 2.85 = 0.15$ , in agreement with the tentatively chosen value 0.144. The uncertainty in log  $K_2$  is probably not higher than 0.03. It should also be observed that the ratio between the constants ( $\log K_1 / K_2 = 2.55$  in 2 M  $\text{teaHClO}_4$  and 2.70 in the 0.5 M medium) are of the order and has as it could be expected the highest value in the medium in which the complexes have the lowest stability.

*Analysis of a basic salt.* One of the solutions (solution 27 in Table 2a) deposited after a few hours a blue crystalline precipitate which was analyzed to have the composition:  $(\text{Nitea})_2(\text{OH})_3\text{ClO}_4 \cdot 3\text{H}_2\text{O}$ . The crystal water was lost on drying and the anhydrous salt was analyzed. Calc. for  $(\text{Nitea})_2(\text{OH})_3\text{ClO}_4$ : Ni 20.73, N 4.94, C 25.4, H 5.8, Cl 6.3. Found: Ni 20.87, N 4.93, C 25.0, H 5.5, Cl 6.4. The weight loss on drying the salt to constant weight at 80 °C

was found to be 16.0 %, and for another preparation 16.4 %. The average weight loss 16.2 % corresponds to 3.03 mol water.

*Discussion of the hydrolysis.* The dominating hydrolysis product of the aqua nickel(II) ion is, according to several investigators,<sup>9-11</sup> the species  $\text{Ni}_4(\text{OH})_4^{4+}$ . The cubane-like structure of  $\text{Ni}_4(\text{OH})_4^{4+}$  has been shown to exist in the complex salt  $\text{Ni}_4(\text{OH})_4\text{tach}_4(\text{NO}_3)_4 \cdot 7\text{H}_2\text{O}$ ,<sup>12</sup> in which tach = 1,3,5-triamine(aaa)-cyclohexane acts as a stereo-specific ligand according to Schwarzenbach.<sup>12</sup> By analogy the hydrolysis product of the  $\text{Ni}(\text{tea})\text{--}(\text{H}_2\text{O})^{2+}$  complex should be  $\text{Ni}_4(\text{OH})_4\text{tea}_4^{4+}$ . However, both our own measurements and those of Cadiot-Smith<sup>4</sup> are in better agreement with the assumption that the dominating hydrolysis product is the diol complex  $[\text{Ni}(\text{tea})_2(\text{OH})_2]^{2+}$  as in the corresponding copper(II) system.<sup>13</sup> This is not unreasonable considering that  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$  can occupy 4 sites in the octahedron leaving only two water molecules in *cis*-position free for hydrolysis.

The data in Table 2 enables us to distinguish between the two possibilities as follows: The stoichiometric concentrations of nickel(II) and triethanolamine can be expressed as eqns. (4) and (5),

$$C_{\text{Ni}} = [\text{Ni}^{2+}] + [\text{Ni}(\text{tea})^{2+}] + [\text{Ni}(\text{tea})_2^{2+}] + \nu[(\text{Ni}(\text{tea})\text{OH}^+)]_v \quad (4)$$

$$C_{\text{tea}} - [\text{tea}]' = [\text{Ni}(\text{tea})^{2+}] + 2[\text{Ni}(\text{tea})_2^{2+}] + 2\nu[(\text{Ni}(\text{tea})\text{OH}^+)]_v \quad (5)$$

where  $\nu$  is either 2 or 4 and  $[\text{tea}]'$  is defined in eqn. (1). By eliminating eqn. (6) from eqns. (4) and (5) by subtraction and employing eqn. (2) we obtain eqn. (7).

$$C'_{\text{Ni}} = [\text{Ni}(\text{tea})_2^{2+}] + \nu[(\text{Ni}(\text{tea})\text{OH}^+)]_v \quad (6)$$

$$[\text{Ni}^{2+}] = \{2C_{\text{Ni}} - (C_{\text{tea}} - [\text{tea}]')\} / (2 + K_1[\text{tea}]) \quad (7)$$

$[\text{Ni}(\text{tea})^{2+}]$  and  $[\text{Ni}(\text{tea})_2^{2+}]$  can now be calculated by eqns. (2) and (3) and the concentration of the hydrolysis product  $C'_{\text{Ni}} = \nu[(\text{Ni}(\text{tea})\text{OH}^+)]_v$  by means of eqn. (6).

Table 2b tabulates data for some of the measured solutions with  $\text{pH} > 7$  which are used for calculating eqns. (8)–(10).

$$\beta_{1,1}^* = (C'_{\text{Ni}}[\text{H}^+]) / [\text{Ni}(\text{tea})^{2+}] \quad (8)$$

$$\beta_{2,2}^* = (0.5 C'_{\text{Ni}}[\text{H}^+]^2) / [\text{Ni}(\text{tea})_2^{2+}]^2 \quad (9)$$

$$\beta_{4,4}^* = (0.25 C'_{\text{Ni}}[\text{H}^+]^4) / [\text{Ni}(\text{tea})_2^{2+}]^4 \quad (10)$$

The values of  $C'_{\text{Ni}}$  are especially high for solutions 26 and 27, and for these solutions it has been necessary before the final calculation to introduce a correction for the change in the initial concentration of  $C_{\text{teaH}^+}$  caused by the hydrolysis (*cf.* the pre-

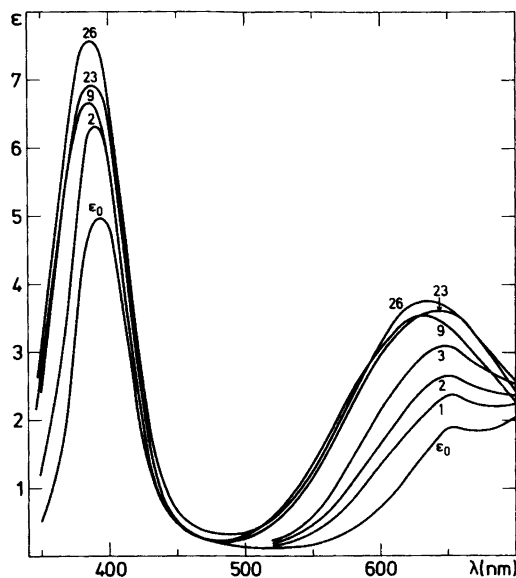


Fig. 2. Spectra ( $\epsilon$ ,  $\lambda$ ) of nickel(II)–triethanolamine perchlorate solutions. The numbers on the curves refer to the corresponding solutions in Tables 1 and 2, and  $\epsilon_0$  to the data for the nickel(II) aqua-ion solutions in Table 3.

ceeding paper<sup>13</sup>). It will be seen from Table 2b that  $\beta_{1,1}^*$  and  $\beta_{2,2}^*$  are much better defined than  $\beta_{4,4}^*$ . A total of nine solutions with different pH and nickel concentration was examined. The mean error on the average values of the  $p\beta^*$ -constants is calculated in the usual manner as  $\sqrt{\Sigma\Delta^2/(n-1)}$ , where  $n$  is the number of determinations and  $\Delta$  are the deviations from the average values of the constants. For comparison the mean errors on the  $p\beta^*$ -constants have to be divided with the degree of polymerization. Paying attention to this fact  $\beta_{1,1}^*$  and  $\beta_{2,2}^*$  have about the same uncertainty. The degree of polymerization is therefore lower than two and the value given for  $p\beta_{2,2}^*$  in Table 2b for this reason somewhat too low. Tentatively we assume it to have the value  $14.8 \pm 0.4$ .

From base titrations at room temperature Cadiot-Smith<sup>4</sup> has estimated the constant

$$\beta_{2,2,2} = [\text{Ni}^{2+}]^2[\text{tea}]^2[\text{OH}^-]^2 / [\text{Ni}_2(\text{tea})_2(\text{OH})_2^{2+}]$$

to be  $10^{-18.2}$ . Employing  $[\text{Ni}(\text{tea})_2^{2+}]$  and  $[\text{H}^+]$  values calculated assuming  $K_1 = 10^{2.85}$  and  $K_w = 10^{-13.73}$  in 0.5 M  $\text{NaClO}_4$ ,<sup>15</sup> respectively, our value for  $\beta_{2,2}^* = 10^{-14.8}$  can be used to calculate for  $\beta_{2,2,2}$ . The value  $10^{-18.4}$  thus obtained is in good agreement with Cadiot-Smith's value.

Table 3. Spectra of  $\text{Ni}(\text{aq})^{2+}$  ( $\epsilon_0$ ),  $\text{Ni}(\text{tea})^{2+}$  ( $\epsilon_1$ ),  $\text{Ni}(\text{tea})_2^{2+}$  and " $\text{Ni}_2\text{tea}_2(\text{OH})_2^{2+}$ " ( $\epsilon_x$ ) in the visible region calculated on basis of the spectra of the following solutions in Tables 1 and 2, Nos. 1, 2, 3, 6, 9 ( $C_{\text{teaH}^+} = 2.00$ ), 14, 23 ( $C_{\text{teaH}^+} = 0.50$ ), 13, 26 ( $C_{\text{teaH}^+} = 0.10$ ,  $C_{\text{Na}^+} = 0.40$ ).

No.		540	560	580	600	620	640	660	680	700 nm
	$\epsilon_0^a$	0.15	0.22	0.41	0.74	1.18	1.68	1.86	1.87	2.03
1	$\epsilon_1$	0.55	1.06	1.86	2.67	3.31	3.44	3.38	2.99	2.73
2	$\epsilon_1$	0.54	1.05	1.84	2.60	3.26	3.53	3.37	3.02	2.73
3	$\epsilon_1$	0.55	1.05	1.85	2.65	3.27	3.53	3.38	3.04	2.71
6	$\epsilon_2$	1.93	2.84	3.50	3.92	3.90	3.70	3.07	2.30	1.58
9	$\epsilon_2$	1.93	2.99	3.61	3.86	3.81	3.56	2.86	2.21	1.51
	$\epsilon_0^b$	0.15	0.21	0.40	0.71	1.15	1.64	1.81	1.84	2.01
14	$\epsilon_1$	0.47	0.98	1.71	2.66	3.36	3.55	3.34	2.99	2.69
13	$\epsilon_1$	0.46	0.94	1.74	2.70	3.38	3.61	3.47	3.05	2.75
23	$\epsilon_x$	2.07	2.94	3.72	4.10	3.47	3.55	3.29	2.68	2.04
26	$\epsilon_x$	1.86	2.81	3.66	4.15	4.47	4.25	3.93	3.28	2.79

<sup>a</sup> Molar extinction coefficients of solution with  $C_{\text{Ni}(\text{ClO}_4)_2} = 0.0629$ ,  $C_{\text{HClO}_4} = 0.02$ ,  $C_{\text{teaHClO}_4} = 2.00$ . <sup>b</sup> Molar extinction coefficients of solution with  $C_{\text{Ni}(\text{ClO}_4)_2} = 0.0524$ ,  $C_{\text{HClO}_4} = 0.02$ ,  $C_{\text{teaHClO}_4} = 0.50$ .

*The absorption spectra.* The absorption curves ( $\epsilon$  versus  $\lambda$ ) for some of the solutions examined and for the aqua nickel(II) ion are shown in Fig. 2. On the basis of these data for a series of wavelengths (some of which are tabulated in Table 3) the molar extinction coefficients for  $\text{Ni}(\text{tea})^{2+}$  ( $\epsilon_1$ ),  $\text{Ni}(\text{tea})_2^{2+}$  ( $\epsilon_2$ ) and for the polymer ( $\epsilon_x$ ) were calculated by means of the general expression for the measured extinction coefficient:

$$\epsilon = \alpha_0 \epsilon_0 + \alpha_1 \epsilon_1 + \alpha_2 \epsilon_2 + \alpha_x \epsilon_x$$

in which  $\alpha_0$ ,  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_x = c_{\text{Ni}}''/c_{\text{Ni}}$  are the fractions of the individual species. The extinction coefficients for  $\text{Ni}(\text{tea})^{2+}$  are obtained directly from the expression:

$$\epsilon_1 = (\epsilon - \alpha_0 \epsilon_0 / \alpha_1) \approx (\epsilon - (1 - \bar{n}) \epsilon_0) / \bar{n}$$

for  $\bar{n}$  values that are not too large.  $\epsilon_2$  is calculated by use of the values obtained for  $\epsilon_1$  and the  $\alpha_n$ -values calculated for solutions 6 and 9 in Table 1. Finally  $\epsilon_x$  is calculated from the  $C_{\text{Ni}}''$ -values and the concentrations of  $\text{Ni}^{2+}$ ,  $\text{Ni}(\text{tea})^{2+}$  and  $\text{Ni}(\text{tea})_2^{2+}$  given in Table 2b. The values obtained for  $\epsilon_1$  and  $\epsilon_2$  are well-defined and it will be seen from Table 3 that the values obtained for  $\epsilon_1$  in 0.5 and 2 M  $\text{teaHClO}_4$  are practically identical. The values obtained for the polymer are not so well-defined, and it is the value for solution 26 which is plotted in Fig. 3. This figure gives the estimated spectra of  $\text{Ni}^{2+}$ ,  $\text{Ni}(\text{tea})^{2+}$ ,

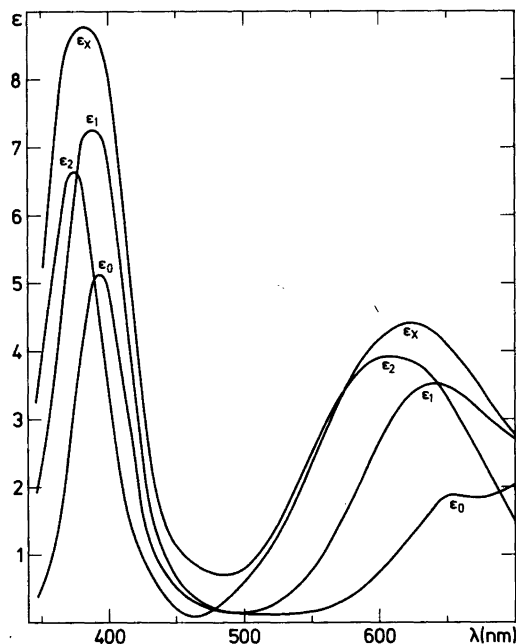


Fig. 3. Spectra ( $\epsilon$ ,  $\lambda$ ) of  $\text{Ni}(\text{aq})_6^{2+}$  ( $\epsilon_0$ ),  $\text{Ni}(\text{tea})^{2+}$  ( $\epsilon_1$ ),  $\text{Ni}(\text{tea})_2^{2+}$  ( $\epsilon_2$ ) and " $\text{Ni}_2\text{tea}_2(\text{OH})_2^{2+}$ " ( $\epsilon_x$ ) drawn on the basis of the data given in Table 3. The curve for  $\epsilon_x$  reproduces the data given for solution 26.

$\text{Ni}(\text{tea})_2^{2+}$  and " $\text{Ni}_2\text{tea}_2(\text{OH})_2^{2+}$ " in the whole wavelength range from 350 to 700 nm.

*Acknowledgement.* The authors thank Dr. Martin Hancock for correcting the English manuscript.

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Received September 30, 1981.