Determination of the Stability Constants of Nitritoborate Ion by Means of an NO_x-Selective Electrode and of Boric Acid Complexes of Acetate and Phthalate by pH Measurement

Derek Midgley
National Power plc, Technology and Environmental Centre, Kelvin Avenue, Leatherhead, Surrey KT22 7SE, UK

The complex between boric acid and nitrite was studied by means of an NO_x-selective gas-sensing membrane electrode and the stability constant found to be $\log \beta = -0.49 \pm 0.02$ at 25 °C. Interaction between boric acid and both acetate and phthalate ions was also observed and stability constants for the complexes of boric acid with acetate, phthalate and hydrogenphthalate were determined from pH measurements at 25 °C to be ($\log \beta$) -0.43 ± 0.03, -0.07 ± 0.02 and ≈ -1, respectively. These measurements enable a revised linear free-energy relationship for boric acid complexes with univalent ions to be calculated. Excluding the less reliable result for hydrogenphthalate, the relationship may be expressed by $\log \beta = -(2.15 \pm 0.58) + (0.45 \pm 0.05)\mathrm{p}K_a$ over a range of seven ligands, with a correlation coefficient of 0.97.

Borax–nitrite solutions have an important application as a cooling medium in auxiliary circuits of nuclear power stations. In the course of analysis of such solutions for chloride with ion-selective electrodes,[1] some anomalous effects were observed in that the electromotive force values were noisier when borax ($Na_2B_4O_7$) was absent. At the pH of measurement the borax would have been converted into boric acid, $B(OH)_3$, which has been shown to form weak complexes with a number of univalent unidentate inorganic ions.[2] A linear free-energy relationship established for these boric acid complexes predicts a stability constant ($\log \beta$) of -0.65 for nitrite, which seems too small to account for the effect. The extent of complexing between nitrite and boric acid was, therefore, studied by means of pH and NO_x-selective electrodes. From the linear free-energy relationship, boric acid complexes with acetate and hydrogenphthalate are predicted to be similar in strength to the nitrite complex and these were studied by means of pH measurements.

Theoretical

By analogy with other inorganic complexes of boric acid, the expected formula of a nitrite complex would be $B(OH)_3NO_2^-$, with a stability constant expressed as in equation (1). The

$$\beta = \{B(OH)_3NO_2^-\}/\{B(OH)_3\}\{NO_2^-\} \qquad (1)$$

activity coefficients of the complex and the nitrite should cancel, especially at the low ionic strengths employed in these experiments, and that of the uncharged boric acid should be unity, hence it is a good approximation to write equation (2), where { } represents activity and [ ] concentration.

$$\beta = [B(OH)_3NO_2^-]/[B(OH)_3][NO_2^-] \qquad (2)$$

For mixtures of sodium nitrite, boric acid and hydrochloric acid (added to adjust the pH to the range 3–5), the charge and mass-balance equations are (3)–(5) where $[OH^-]$ and $[B(OH)_4^-]$ have been neglected because of the low pH. The

$$[Na^+] + [H^+] = [NO_2^-] + [B(OH)_3NO_2^-] + [Cl^-] \qquad (3)$$

$$\text{Total boron, } T_B = [B(OH)_3] + [B(OH)_3NO_2^-] + [B(OH)_4^-] \approx [B(OH)_3] + [B(OH)_3NO_2^-] \qquad (4)$$

$$\text{Total nitrite, } T_N = [NO_2^-] + [HNO_2] + [B(OH)_3NO_2^-] \qquad (5)$$

NO_x electrode responds to free nitrous acid, HNO_2, the concentration of which is related to the nitrite concentration by the dissociation constant, K_a [equation (6)], where f_1 is the

$$K_a = \{H^+\}[NO_2^-]f_1/[HNO_2] \qquad (6)$$

activity coefficient for a univalent ion and $\{H^+\}$ is the hydrogen-ion activity measured by a glass electrode. Hence, from equation (6) we obtain (7), from equations (5) and (7), (8) and from

$$[NO_2^-] = [HNO_2]K_a/\{H^+\}f_1 \qquad (7)$$

$$[B(OH)_3NO_2^-] = T_N - [HNO_2](1 + K_a/\{H^+\}f_1) \qquad (8)$$

$$[B(OH)_3] = T_B - T_N + [HNO_2](1 + K_a/\{H^+\}f_1) \qquad (9)$$

equations (4) and (8), (9). Thus the concentrations required for equation (2) can be expressed in terms of the known quantities T_N, T_B and K_a, the measured quantities $[HNO_2]$ and $\{H^+\}$ and the activity coefficient f_1, which can be calculated from the Davies equation $-\log f_1 = 0.511[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.3I]$ for a univalent ion at 25 °C. In this instance, all the ions in solution are univalent and thus the ionic strength, I, is given by $I = [Na^+] + [H^+] \approx T_N + \{H^+\}$. Thus an almost perfect analytical solution of equation (2) is possible and the experimental conditions were maintained such that the approximations introduced a negligible error.

Calculation from pH *Measurements.—Monoprotic acids.* Equations (1)–(9) are still valid, but instead of $[HNO_2]$ being measured directly, it was obtained [equation (10)] by

$$[HNO_2] = T_N - [Na^+] - \{H^+\}/f_1 + [Cl^-] \qquad (10)$$

subtracting equation (3) from (5). The equations for acetate complexing are the same, except that $[HO_2CMe]$ and

$[O_2CMe^-]$ are substituted for $[HNO_2]$ and $[NO_2^-]$, respectively. The complex would be $B(OH)_3(O_2CMe)^-$.

Diprotic acids. Consider a diprotic acid, H_2A, with first and second dissociation constants K_{a1} and K_{a2}, respectively. The acid is added as its potassium salt, KHA, and hydrochloric acid or sodium hydroxide may also be added. The mass and charge-balance equations, neglecting $[OH^-]$ and $[B(OH)_4^-]$ as above, are (11)—(14), where $\beta_{11} = \{B(OH)_3HA^-\}/\{B(OH)_3\}\{HA^-\}$.

$$\text{Total boron, } T_B = [B(OH)_3] + [B(OH)_3HA^-] + [B(OH)_3A^{2-}] \quad (11)$$

$$\text{Total ligand, } T_A = [H_2A] + [HA^-] + [A^{2-}] + [B(OH)_3HA^-] + [B(OH)_3A^{2-}] \quad (12)$$

$$[K^+] + [Na^+] + [H^+] = [Cl^-] + [HA^-] + 2[A^{2-}] + [B(OH)_3HA^-] + 2[B(OH)_3A^{2-}] \quad (13)$$

$$[HA^-] = \frac{(2T_A + [Cl^-] - [H^+] - [Na^+] - [K^+])}{(1 + 2K_{a1}[H^+] + \beta_{11}[B(OH)_3])} \quad (14)$$

In the first instance, β_{11} was estimated from K_{a1} and the linear free-energy relationship shown in Fig. 2 and $\{B(OH)_3\} \approx T_B$; $[HA^-]$ was then used to calculate $[H_2A]$ and $[A^{2-}]$ from the pH and dissociation constants, so that a refined value of $[B(OH)_3]$ can be obtained. Iteration through equations (14)–(17) occurred until a consistent value of β_{01} was obtained.

$$[B(OH)_3] = T_B - T_A + [H_2A] + [HA^-] + [A^{2-}] \quad (15)$$

$$[B(OH)_3A^{2-}] = T_B - \beta_{11}[B(OH)_3][A^{2-}] \quad (16)$$

$$\beta_{01} = [B(OH)_3A^{2-}]/[A^{2-}][B(OH)_3] \quad (17)$$

The value of β_{11} was then changed systematically until the value giving the smallest relative standard deviation in β_{01} was found and this pair of stability constants was accepted as giving the best approximate description of the system, as has been done previously for systems of weak complexes.[3] In the system studied, H_2A represents phthalic acid, $C_6H_4(CO_2H)_2$.

Experimental

Apparatus.—Potentials were measured on an Orion 940 digital pH meter reading to 0.1 mV and displayed on a chart recorder so that the approach to equilibrium could be checked. An Ingold S5102 combination electrode was used to measure pH and an Orion 95-10 ammonia electrode was converted into an NO_x-selective electrode by changing its filling solution, as below. The temperature was controlled at 25.0 °C by means of a Techne TU-16 controller and RB-5 refrigeration unit. Water from the thermostat was pumped round a water-jacketed glass cell with a close-fitting lid holding the electrodes.

Reagents.—All reagents were of analytical grade (BDH). The standard NIST buffers used to calibrate the pH electrode were 0.05 mol kg^{-1} potassium hydrogenphthalate and 0.025 mol kg^{-1} potassium dihydrogenphosphate + 0.025 mol kg^{-1} disodium hydrogenphosphate. 1 mol l^{-1} Hydrochloric acid and 1 mol l^{-1} sodium hydroxide solutions were prepared by dilution of Con-Vol ampoules. A stock 0.1095 mol l^{-1} sodium nitrite solution was prepared.

The ionic strength adjustment buffer recommended by Orion for use with the NO_x electrode was prepared by dissolving 19.0 g of anhydrous sodium sulphate in about 50 cm^3 of water, adding 5.3 cm^3 of concentrated sulphuric acid and making up to 100 cm^3 with water. This solution was added to the test solution in 1:10 proportions.

Electrode filling solution. The Orion 95-10 electrode was filled with a solution of 0.1 mol l^{-1} sodium chloride and 0.05 mol l^{-1} sodium nitrite to convert it into a NO_x electrode.

Procedure.—Before each run, the pH electrode was calibrated in first 1:1 phosphate buffer (pH 6.865) and then phthalate buffer (pH 4.005).

Nitrite complexes. Deionized water (100 cm^3) was pipetted into the water-jacketed glass cell, followed by an appropriate quantity (typically 0.01–0.02 cm^3) of 1 mol l^{-1} hydrochloric acid, depending on the pH range required. The electrodes were rinsed thoroughly with deionized water, dried with a tissue and immersed in the solution, which was left to attain thermal equilibrium. The solution was stirred continuously by a magnetic stirrer bar. The depth of immersion of the NO_x electrode and its position relative to the stirrer were kept constant throughout the run, otherwise spurious shifts in potential occurred.

Portions (typically 0.5 or 1 cm^3) of stock sodium nitrite solution were pipetted into the beaker and in each case the steady readings from the NO_x and pH electrodes were noted. Further 0.01 cm^3 portions of hydrochloric acid solution were added when pH adjustment was required. The results from this part of the run were used to provide an internal calibration for the NO_x electrode.

Solid boric acid was then added to the above solution in portions of approximately 0.35 g, the exact weight being determined by difference. The steady readings from both electrodes were noted. The solubility of boric acid allowed three or four additions to be made and portions of this size were required to produce significant differences in electromotive force (0.3–0.7 mV). Occasionally, further portions of hydrochloric acid were added to vary the pH. The results from this part of the run were used to calculate the stability constant.

Acetate and phthalate complexes. The procedure was essentially the same as above, without the NO_x electrode and with acetate or phthalate solutions instead of nitrite. Acetate runs started with 100 cm^3 of 0.01 mol l^{-1} acetic acid + 0.01 mol l^{-1} sodium acetate buffer: in one run, no other acid or base was added, in a second 0.1 cm^3 of 1 mol l^{-1} hydrochloric acid was added after the first boric acid addition and in the third 0.1 cm^3 of 1 mol l^{-1} sodium hydroxide was added after the first boric acid addition. The phthalate studies started with 100 cm^3 of 0.05 mol kg^{-1} (0.049 55 mol l^{-1}) potassium hydrogenphthalate (which was also used to calibrate the electrode) and in some runs additions of 0.5 cm^3 of 1 mol l^{-1} hydrochloric acid or 1 mol l^{-1} sodium hydroxide were made after the initial boric acid addition.

Results

NO_x-Electrode Calibration.—The slope factor of the NO_x electrode was 55 ± 1 mV per decade, *i.e.* slightly below the Nernstian value of 59 mV per decade, but within the limits expected for such electrodes. Deviation from linearity occurred for $\log[HNO_2] < -4.3$ and stability constants were calculated only with data from the linear region. Fig. 1 shows two

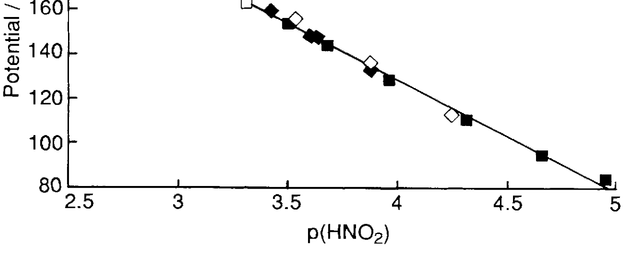

Fig. 1 Calibrations at different pH and ionic strength: ■, potassium hydrogenphthalate (pH 4); □, Orion (pH 1.35); ◆, dilute (pH 4.4); ◇, dilute (pH 3.9); —, least squares

Table 1 Stability constant of nitritoborate complex ion from NO_x electrode measurements

Run	[Nitrite]/ mmol l^{-1}	[Borate]/ mmol l^{-1}	pH	β/l mol^{-1}	s.d.*/ l mol^{-1}
1	2.1–3.2	49–154	3.6–4.3	0.376	0.066 (5)
2	2.15	109–173	4.34	0.370	0.105 (2)
3	4.2	63–209	4.0–4.6	0.353	0.083 (7)
4	4.2	119–240	3.9	0.263	0.066 (3)
5	7.6–9.9	60–290	4.0	0.242	0.023 (6)
6	9	46–302	4.4	0.350	0.067 (5)
			mean	0.324	
			s.d.*	0.081(28)	
			s.d. of mean	0.015	

* Standard deviation for a single result (number of results in parentheses).

Table 2 Results for run 3 of Table 1; [nitrite] = 4.21 mmol l^{-1}

		Measurements		
[Borate]/ mmol l^{-1}	[HCl]/ mmol l^{-1}	$p(HNO_2)$	pH	β/l mol^{-1}
63	0.189	3.823	4.538	0.46
117	0.189	3.817	4.530	0.31
117	0.284	3.657	4.354	0.46
117	0.378	3.538	4.231	0.40
209	0.378	3.538	4.226	0.28
209	0.473	3.446	4.125	0.29
209	0.567	3.365	4.037	0.28
			mean	0.35
			s.d.	0.08

Table 3 Stability constant of nitritoborate complex from pH measurements

Run	β/l mol^{-1}	s.d.*/l mol^{-1}	pK_a
1	0.279	0.078	3.207
2	0.333	0.134	2.879
3	0.297	0.234	3.188
4	0.115	0.029	3.195
5	0.111	0.015	3.234
6	0.244	0.091	3.219
mean	0.244		3.154
s.d.*	0.091		0.136
s.d. of mean	0.017		0.055

* Numbers of results as in Table 1.

calibrations in dilute solution at different pH and also two calibrations at constant ionic strength in a background of either potassium hydrogenphthalate buffer (0.05 mol l^{-1}) or the ionic strength adjustment buffer recommended by Orion for NO_x determination (pH 1.35, $I = 0.6$ mol l^{-1}). The agreement between calibrations in different media suggests that osmotic effects on the electrode are negligible.

Nitrite Stability Constants.—The stability constants calculated from the measurement of pH and free nitrous acid concentration are shown in Table 1 for six runs under different conditions; expressed as log β, the global mean is -0.49 and has a standard deviation of 0.02. When stability constants are so small, particular care must be taken to avoid spurious results arising from unconsidered effects. In the present case the following precautions were taken.

(1) The NO_x electrode was calibrated internally within each run and showed excellent consistency in slope factor and standard potential between runs. Moreover, the agreement between calibrations in different constant background media (above) suggests that osmotic effects on the electrode were negligible and that variations in osmolarity during the experiments were of no consequence. Attempts at measurement in a background of constant pH and ionic strength were unsuccessful because the phthalate ion in the pH buffer also complexed the boric acid (see below).

(2) The total nitrite concentration was varied over an approximately five-fold range between runs and by up to 50% within some individual runs, without affecting the results.

(3) The pH was varied within and between runs. Although measurements at pH $\leqslant 3.5$ were unreliable because of loss of volatile nitrous acid, no trends were discernible in the range pH 3.5–4.6. Results from a typical run are shown in Table 2.

(4) Changing to a fresh stock nitrite solution made no difference to the calibration or stability constants.

(5) The calculations are almost insensitive to the value of the nitrite protonation constant. Changing from the currently accepted[4] best value of $pK_a = 3.15$ to the previously accepted $pK_a = 3.29$ changed the stability constant only in the third decimal place, which is experimentally insignificant.

(6) The results were recalculated, using only the pH data, which is the method most commonly used for determining stability constants, because selective electrodes are not generally available for the reactants involved. The results in Table 3 show fair agreement with those obtained above, but are very sensitive to the value of K_a. The protonation constant was varied empirically until the solution before addition of boric acid showed only a small ($< 10^{-8}$ mol l^{-1}) residual in the nitrite mass balance and that value of K_a was used for the calculations in that run. The mean value of pK_a for all the runs, however, is close to the accepted value of 3.15; some of the uncertainty in the value of K_a is likely to arise from variations in liquid-junction potentials and treatment of activity coefficients between the two sets of measurements. The results in Table 1 make fuller use of the data and should be more reliable than those in Table 3, which do, however, indicate that the apparent stability constant is not merely an artifact arising from anomalous behaviour of the NO_x electrode. The pH methodology was checked further by studying solutions of boric acid and organic buffers.

Acetate Stability Constants.—The results for acetate, with a very well established pK_a of 4.756, are given in Table 4 and show that fairly good precision for small stability constants can be obtained by the pH method. The mean stability constant of acetatoborate ion so obtained was log $\beta = -0.43$, with a standard deviation (13 results) of 0.03.

Phthalate Stability Constants.—Results for phthalate complexes are more difficult to interpret, because of the possibility of forming complexes between boric acid and both phthalate and hydrogenphthalate ions. Calculations on the basis that only the latter was involved produced absurd results (*e.g.* negative concentrations). There is no analytical solution for the calculation of stability constants of simultaneously formed protonated and unprotonated complexes of the same ligand, when only mass balances and pH data are available, so an iterative process had to be used. An initial value of $\beta_{11} = 0.15$ l mol^{-1} was estimated from the linear free-energy relationship reported by Bousher *et al.*[2] and used to calculate β_{01} for all data points; β_{11} was then varied systematically until a minimum in the relative standard deviation for β_{01} was obtained.

A problem occurred, however, in that with the accepted values of $pK_{a1} = 2.95$ and $pK_{a2} = 5.408$ for phthalic acid it was impossible to obtain residual errors of less than 10^{-4} mol l^{-1} in the mass balance for total phthalate in the absence of boric acid. Varying pK_{a1} until the residual error was $< 10^{-6}$ mol l^{-1} resulted in inconsistent values of β_{01}, which were negative at pH > 4. With pK_{a1} held constant at 2.95, pK_{a2} was varied until the residuals were considered sufficiently small ($\approx 10^{-7}$ mol l^{-1}) and the value 5.3944 was adopted for the calculations.

Table 4 Stability constant of acetatoborate

Run	Boric acid added/g[a]	pH	β/ l mol^{-1}
1	0.0000	4.712	
	0.3024	4.705	0.360
	0.6048	4.696	0.389
	0.9052	4.691	0.345
2	0.0000	4.714	
	0.3005	4.705	0.363
	0.3005[b]	4.616	0.472
	0.6003[b]	4.607	0.448
	0.8979[b]	4.601	0.414
	1.1949[b]	4.594	0.399
3	0.0000	4.715	
	0.2980	4.708	0.198
	0.2980[c]	4.791	0.339
	0.5929[c]	4.782	0.383
	0.8915[c]	4.773	0.399
	1.1882[c]	4.767	0.387
		mean	0.377
		s.d.	0.066
		s.d. of mean	0.018

[a] Per 100 cm^3 of 0.01 mol l^{-1} acetic acid–0.01 mol l^{-1} sodium acetate. [b] With a total addition of 0.1 cm^3 of 1 mol l^{-1} HCl. [c] With a total addition of 0.1 cm^3 of 1 mol l^{-1} NaOH.

Table 5 Determination of boric acid–phthalate stability constants from pH measurements (with β_{11} = 0.1 l mol^{-1}, pK_{a1} = 2.95, pK_{a2} = 5.3944)

Additions per 100 cm^3[a]				
Boric acid/g	HCl[b] cm^3	NaOH[b] cm^3	pH	β_{01}/ l mol^{-1}
0.3775	0.0	0.0	3.997	0.648
0.7495	0.0	0.0	3.998	0.666
1.1051	0.0	0.0	3.980	0.690
0.2996	0.0	0.0	3.996	0.837
0.5971	0.0	0.0	3.988	0.856
0.8973	0.0	0.0	3.979	0.872
0.2989	0.0	0.0	3.996	0.839
0.5984	0.5	0.0	3.683	0.709
0.8979	0.5	0.0	3.676	0.920
1.1975	0.5	0.0	3.669	1.040
0.2969	0.0	0.0	3.995	1.017
0.2969	0.0	0.5	4.295	1.126
0.5994	0.0	0.5	4.286	0.880
0.9021	0.0	0.5	4.276	0.846
1.1990	0.0	0.5	4.265	0.839
			mean	0.852
			s.d.	0.138

[a] 0.05 mol l^{-1} potassium hydrogenphthalate solution. [b] 1 mol l^{-1} solution.

This difference from the literature value is likely to arise from differences in liquid-junction potentials and in the treatment of activity coefficients. With pK_{a1} = 2.95 and pK_{a2} = 5.3944, the minimum in the relative standard deviation of β_{01} occurred at β_{11} = 0.10 l mol^{-1}; results calculated with this set of constants are shown in Table 5. The value obtained for β_{01} was not very dependent on β_{11}; a variation of ±0.05 l mol^{-1} in β_{11} produced a change of ±0.01 l mol^{-1} in both β_{01} and its standard deviation. A change of 0.0001 in pK_{a2}, however, produced changes of 0.03 l mol^{-1} in β_{11}, but <0.001 l mol^{-1} in its standard deviation and 0.75 µmol l^{-1} in the residual mass balance. The sensitivity of the phthalate results to variations in pK_{a2} far smaller than the uncertainty in its experimental value means that the standard deviation in Table 5 probably understates the uncertainty in the value of β_{01} and neither β_{01} nor β_{11} can be regarded as being as reliable as the constants for nitritoborate or acetatoborate.

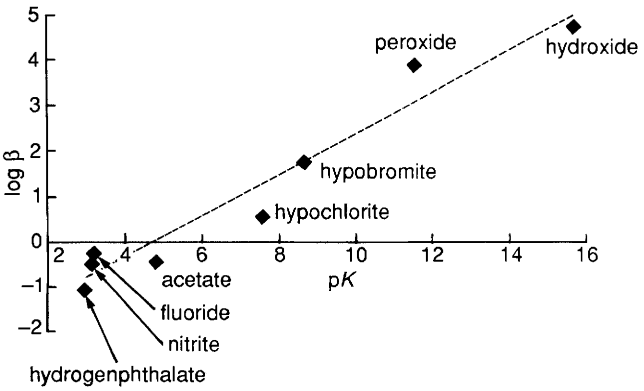

Fig. 2 Linear free-energy relationship between the stability constant (β) and the acid dissociation constant (pK) of singly charged unidentate ligands of boric acid, showing the least-squares fit of the data

Discussion

The value of log β = -0.49 ± 0.02 for the nitritoborate complex measured by means of the NO$_x$-selective electrode is in good agreement with the -0.65 predicted from the previous[2] linear free-energy relationship. With this constant, the nitritoborate complex would account for about 0.6% of the total nitrite in the acidified borax–nitrite solutions taken for chloride analysis, which seems too small to explain the observed protective effect of borate on silver–silver chloride electrodes in nitrite media.

Stability constants for boric acid complexes of acetate [log β = -0.43 ± 0.03 (13 results)], hydrogenphthalate (log $\beta \approx -1.0$) and phthalate [log β = -0.07 ± 0.02 (15 results)] were calculated by the pH method and a revised linear free-energy relationship for all known boric acid complexes with univalent ions is shown in Fig. 2. Excluding the less reliable result for hydrogenphthalate, the relationship may be expressed by equation (18) with a correlation coefficient of 0.97.

$$\log \beta = -(2.15 \pm 0.58) + (0.45 \pm 0.05)\mathrm{p}K_a \quad (18)$$

Aqueous borate chemistry is, in general, complicated by the formation of polyborates, but in the pH range (3.6–4.7) relevant to this work Raman spectra show only the B(OH)$_3$ peak,[5] which is also consistent with other methods of investigation. At pH 8 ± 2 polyborates constitute a significant fraction of the total boron[5] and the study of borate complexes would be correspondingly more complicated.

Acknowledgements

I thank Mr. C. Gatford for making some of the pH measurements. This work is published by permission of National Power.

References

1 D. Midgley and C. Gatford, *Microchem. J.*, 1990, **42**, 225.
2 A. Bousher, P. Brimblecombe and D. Midgley, *J. Chem. Soc., Dalton Trans.*, 1987, 943.
3 H. S. Dunsmore and D. Midgley, *J. Chem. Soc., Dalton Trans.*, 1972, 64.
4 R. M. Smith and A. E. Martell, *Critical Stability Constants*, Plenum, New York, 1976, vol. 4.
5 J. Farmer, *Chem. Ind.* (*London*), 1982, 145.

Received 17*th October* 1990; *Paper* 0/04667A