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Determination of Hydroxide Ion Concentration by Measurements with a Lead Amalgam Electrode. Plumbate and Borate Equilibria in Alkaline 3.0 M NaCl-Medium: Absence of Monoborate (–2) and (–3) Ions

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Using a lead amalgam electrode (denoted with (I) in the text below) the complex formation at 25°C between Pb^{2+} and OH^- has been studied in alkaline 3.0 M Na(Cl) medium. The medium ion Cl^- does not seem to play any important role for formation of the $Pb^{2+}-OH^-$ complexes and the formula of the species in 3.0 M Na(Cl) are the same as those found earlier in 3.0 M $Na(ClO_4)$ by Carell and Olin.[1] The following equilibrium constants were deduced for 3.0 M Na(Cl),

$$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2 \qquad \log \beta_2 = 7.783 \pm 0.035$$
$$Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^- \qquad \log \beta_3 = 9.962 \pm 0.003$$

The constants have been refined using the generalized least squares program LETAGROPVRID [2] and the error given is 3σ (σ is the standard deviation).

In the second part of the work the lead amalgam electrode has been used for measuring equilibrium concentrations of OH^- in strongly alkaline borate solutions.

In the $[OH^-]$-range, 0.007–0.500 M, there was no evidence for formation of mononuclear borate ions of higher negative charge than $B(OH)_4^-$ (for instance $H_2BO_3^{2-}$ or BO_3^{3-}).

The complex formation between Pb^{2+} and OH^- in alkaline 3.0 M $NaClO_4$-medium has been studied by Carell and Olin.[1] They measured the concentration of Pb^{2+} by using a cell,

$$\text{Pb(in Hg)} \mid B \text{ M } Pb(ClO_4)_2,\ A \text{ M NaOH},\ (3.0-A)NaClO_4 \mid \text{ref.} \qquad \text{(I)}$$

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The emf of this cell may be written

$$E = E_0 - 29.578 \log [Pb^{2+}] + E_j \quad (1)$$

where E_0 is a constant and E_j the liquid junction potential. The measurements showed that the lead(II)-complexes present in alkaline 3.0 M $Na(ClO_4)$-medium are $Pb(OH)_2$ and $Pb(OH)_3^-$ and the following formation constants were given,

$$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2 \qquad \log \beta_2 = 10.9 \pm 0.1$$
$$Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^- \qquad \log \beta_3 = 13.66 \pm 0.05$$

In the range studied ($-2.5 < \log[OH^-] < -0.5$) they found that Z, the average number of OH^- bound per Pb^{2+} was very close to 3 (varied between 2.90 and 2.97). It means that in this range $Pb(OH)_3^-$ is the main species and the conditions for B, the total lead concentration may be simplified to $B = \beta_3[Pb^{2+}][OH^-]^3$. Eliminating $[Pb^{2+}]$ from this expression and inserting in (1) gives (E_0' = constant for constant B)

$$E = E_0' + 3 \times 29.578 \log[OH^-] + E_j(OH^-) \quad (2)$$

From this equation we see that it would be possible to use a calibrated lead amalgam electrode for measuring $[OH^-]$, thus to use it in the same way as a hydrogen electrode. From eqn. (2) we also see that the accuracy of this electrode is 1.5 times that of a hydrogen electrode and consequently would be very useful for measuring $[OH^-]$ in rather strong alkaline solutions where other electrodes fail.

The experiments of the present work were carried out in 3.0 M Na(Cl)-medium. In the first part of our study we aimed to investigate whether $Pb(OH)_2$ and $Pb(OH)_3^-$ are the main complexes in 3.0 M Na(Cl)-medium also and, if so, to determine their formation constants. In the second part of the investigation the lead amalgam electrode was used for measuring equilibrium concentrations of OH^- in strongly alkaline borate solutions. In our earlier studies [3] on borate equilibria, using a hydrogen electrode, there was no evidence for the existence of borate ions with more negative average charge per boron than -1 (formation of complexes $B(OH)_4^-$, ($H_2BO_3^-$) or ($(B(OH)_4)_n^{n-}$). However from "pH"-studies by using indicators Konopik and Leberl [4] have proposed that "$H_2BO_3^-$" should split off two more protons with pK_a-values of -12.3 and -13.4. Also Hahn and Klockmann [7] claimed to have found two additional dissociation steps of boric acid with the pK_a-values -12.74 and -13.8 to -13.5. By using an amalgam electrode it will be possible to study rather alkaline borate solutions and by using this electrode we hope to get further information whether higher charged borate ions are present or not.

REAGENTS AND ANALYSIS

Sodium chloride, Merck *p.a.* was used. We found that this product was of high purity and could be used after drying at 350°C without further purification. *Hydrochloric acid*, the ordinary KEBO *p.a.* product was used. The acid was standardized against $KHCO_3$ and Tl_2CO_3, the results agreed within $\pm$ 0.1 %.

Sodium hydroxide was prepared and analysed as described in Ref. 3.

Lead (II)perchlorate solutions and *lead amalgam* were prepared and analyzed as described by Carell and Olin.[1] A new amalgam was prepared for every titration.

Borate solutions were prepared from recrystallized borax. The crystalline borax was stored according to the directions given by Kolthoff.[5]

Apparatus. Like in our previous studies[3] in alkaline solutions, Jena Geräte glass was used for titration vessels and burets. The electrode vessel and the salt bridge were of the same type as described in Ref. 3. The amalgam emf was read to $\pm$ 0.01 mV by a Cambridge potentiometer. The silver-silver chloride reference electrode cell was prepared by Brown's method.[6] The cells including the titration vessel were kept in an oil thermostat at 25°C. During the titrations the equilibrium solution was stirred by means of commercial nitrogen, freed from O_2 by bubbling through an alkaline solution of pyrogallol. The incoming gas was purified and saturated with water as described in Ref 3.

PROCEDURE

The present investigation was carried out as a series of potentiometric titrations at 25°C. As ionic medium 3.0 M Na(Cl) was used. The composition of the solutions measured may be written,

$$S = B\ Pb(ClO_4)_2,\ A\ M\ NaOH,\ C\ M\ B(OH)_3,\ (3.0-A)\ M\ NaCl$$

The analytical sodium hydroxide and boric acid concentrations were varied between 0.007—0.500 M and 0.000—0.050 M, respectively, and the analytical lead concentration was kept between 1 and 6 $\times$ 10^{-4} M. The "free" lead concentration $[Pb^{2+}]$ was measured with the cell,

$$-Pb(in\ Hg)\ |\ S\ |\ RE+ \qquad (II)$$

where S is the equilibrium solution and RE a reference half-cell. The reference half-cell used was

RE = 3.0 M NaCl | 3.0 M NaCl-solution saturated with AgCl | Ag,AgCl.

Assuming the activity factors to be constant, the emf of the cell (II) may be written,

$$E = E_0 - 29.578 \log [Pb^{2+}] + E_j \qquad (3)$$

where E_0 is a constant and E_j the liquid junction potential.

If we consider reactions

$$Pb^{2+} + nCl^- + pOH^- \rightleftharpoons PbCl_n(OH)_p^{2-(n+p)}$$

the mass balance and the law of mass action give the equations

$$B = [Pb^{2+}] + \sum\sum \beta_{p,n}'[Pb^{2+}][Cl^-]^n[OH^-]^p \qquad (4a)$$

$$A = [OH^-] + \sum\sum p\beta_{p,n}'[Pb^{2+}][Cl^-]^n[OH^-]^p \qquad (4b)$$

$$X = [Cl^-] + \sum\sum n\beta_{p,n}'[Pb^{2+}][Cl^-]^n[OH^-]^p \qquad (4c)$$

where $\beta_{p,n}' = [PbCl_n(OH)_p][Pb^{2+}]^{-1}[Cl^-]^{-n}[OH^-]^{-p}$

$A = [OH^-]_{tot}$ = the analytical concentration of the ligand A. $X = [Cl^-]_{tot}$ = the analytical concentration of the medium ligand X. $B = [Pb^{2+}]_{tot}$ = the analytical concentration of the central atom B.

As in the present case, Cl^- is a medium ion, its concentration changes very little during a titration and the quantities $\beta_{p,n}'[Cl^-]^n$ may be considered as constants and eqns. (4a), (4b), and (4c) may then be rewritten in the following way

$$B = b + \sum \beta_p b a^p \text{ (5a)}, \quad A = a + \sum p\beta_p b a^p \text{ (5b)}, \quad X = x + \sum n\beta_p b a^p \text{ (5c)}$$

where $\beta_p = \sum \beta_{p,n}'[\text{Cl}^-]^n$, $b = [\text{Pb}^{2+}]$, $a = [\text{OH}^-]$ and $x = [\text{Cl}^-]$.

The approximations made in deducing eqns. (5a), (5b), and (5c) are the same as those always made when the "medium method" is used. It means chemically that the measurements of the present work only give the number of OH^- in the complexes but no information about the number of bound Cl^--ions. Thus one may have a number of complexes, *e.g.* $Pb(OH)_2$, $PbCl_2(OH)_2^{2-}$, $PbCl_3(OH)_2^{3-}$, $PbCl_n(OH)_2^{n-}$, which in our measurements will be equivalent to a single complex $PbCl_n(OH)_2^{n-}$. As usual in the "medium method" we write all complexes with the same number of OH^- as a single complex $Pb(OH)_p^{2-p}$.

All titrations were started from an acid solution with known total lead concentration, B, and alkali was added from a buret. As long as $[H^+] \geq 10^{-5}$ the concentration of the $Pb(OH)_p$-complexes can be neglected compared with B and expression (4a) is then reduced to

$$B = [\text{Pb}^{2+}] + \sum \beta_n [\text{Pb}^{2+}][\text{Cl}^-]^n \tag{6}$$

Eliminating $[Pb^{2+}]$ from (6) and inserting in (3) gives

$$E = E_0' + 29.578 \log (1 + \sum \beta_n [\text{Cl}^-]^n) - 29.578 \log B + E_j \tag{7}$$

From a plot $(E + 29.578 \log B)$ against $[H^+]$ the constant $E_0 = E_0' + 29.578 \log (1 + \sum \beta_n [\text{Cl}^-]^n)$ was obtained by extrapolation to $[H^+] = 0$. After this E_0-determination on the acid side so much OH^--ions were added that the lead hydroxide was precipitated and still more until all hydroxide became completely dissolved. Then the titration was continued and emf was measured up to $[OH^-] = 0.200$ M.

Now from the known quantities E_0, B and the measured emf we could calculate

$$\eta = \log B/b = \log (1 + \sum \beta_p a^p) \tag{8}$$

The concentrations of Pb^{2+} in the measured solutions are very small and we therefore have $B = \sum \beta_p b a_p$ and $\eta = \log \sum \beta_p a^p$ and from (8) we find

$$\frac{d\ \eta}{d \log a} = \frac{\sum p\ \beta_p a^p}{\sum \beta_p a^p} = Z \tag{9}$$

CALCULATIONS

p and β_p for the complexes $Pb(OH)_p^{2-p}$. Since log $[OH^-]$ was not measured it had to be calculated. For this calculation we used the method developed by Leden. With our notations we have $\delta\eta/\delta \log a = Z$, and $a = A - BZ$. Neighboring points were used to find $\Delta\eta/\Delta(\log [OH^-])$ and as a first guess of a, $(A - 3B)$ was used. The successive approximations were repeated till log a did not change on a further calculation. The data plotted as η (log $[OH^-]$) fall on a

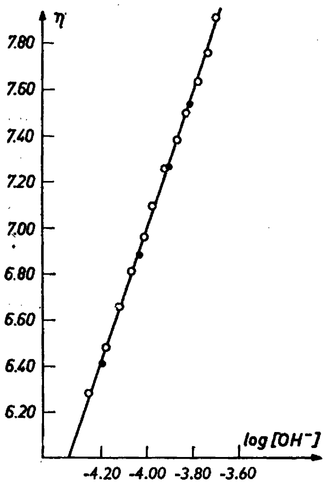

Fig. 1. $\eta = \log [Pb(II)]_{tot}/[Pb^{2+}]$ as a function of log $[OH^-]$. The solid line is calculated with $\log \beta_2 = 7.783$ and $\log \beta_3 = 9.962$.

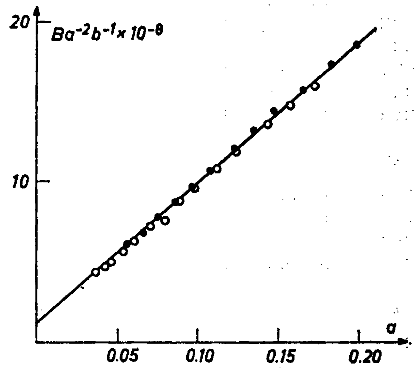

Fig. 2. $[Pb(II)]_{tot}/([Pb^{2+}][OH^-]^2)$ as a function of $[OH^-]$. The straight line gives $\log \beta_2 = 7.87 \pm 0.10$ and $\log \beta_3 = 9.95 \pm 0.10$.

○ Titration 1, ● titration 2.

single curve as seen from Fig. 1. The slope of the curve was around 2.95. From this fact it seems likely that the species present are the same as those found in 3.0 M $NaClO_4$ medium. Thus, we assumed formation of $Pb(OH)_2$ and $Pb(OH)_3^-$ with the formation constants β_2 and β_3. In order to test this assumption we plotted $Ba^{-2}b^{-1}$ against a. If the hypothesis is valid, β_2 is found from the intercept on the $Ba^{-2}b^{-1}$ axis and β_3 from the slope of the straight line obtained. The presence of other complexes should make the line bend upwards or downwards. From the plot shown in Fig. 2 we see that a straight line through the points is a rather good approximation. From the plot the following equilibrium constants were calculated,

$$\log \beta_2 = 7.87 \pm 0.10 \text{ and } \log \beta_3 = 9.95 \pm 0.10$$

These graphically determined constants were then refined by using the least squares program LETAGROPVRID.[2] The input experimental data were B, A, and E and the first graphical estimated set of constants E_0 (the value of E_0 is different for different titrations), β_2 and β_3. It has been assumed that A and B are without errors and that all errors are on E. In LETAGROPVRID the computer then searches the values of the constants E_0, β_2, and β_3 that minimize the error squares sum

$$U = \sum (E_{calc} - E_{obs})^2 = \sigma^2(E) \cdot (\text{degree of freedom}) \quad (11)$$

where $\sigma(E)$ is the standard deviation in E, the measured emf value. We found the following best set of constants

Table 1. Data for lead amalgam titration in 3.0 M Na(Cl). $B = [Pb(II)]_{tot}$, $A = [OH^-]_{tot}$ and $C = [B(III)]_{tot}$ are given in mM and E in mV.

Titration 1. $E_0(1) = 396.36 \pm 0.05$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.5593,	58.028,	0,	678.00,	−0.38;	0.5453,	68.152,	0,	684.05,	+0.03;
0.5320,	77.783,	0,	689.49,	−0.05;	0.5185,	87.551,	0,	694.39,	−0.12;
0.5034,	98.525,	0,	699.19,	−0.04;	0.4883,	109.405,	0,	703.50,	+0.02;
0.4674,	124.559,	0,	708.94,	+0.07;	0.4513,	136.229,	0,	712.97,	−0.11;
0.4334,	149.214,	0,	716.90,	−0.07;	0.4090,	166.864,	0,	721.67,	+0.13;
0.3849,	184.284,	0,	726.13,	+0.20;	0.3635,	199.760,	0,	729.80,	+0.31;

Titration 2. $E_0(2) = 397.14 \pm 0.29$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.3415,	154.86,	0,	720.98,	−0.80;	0.3270,	125.378,	0,	713.50,	−0.70;
0.3116,	93.970,	0,	702.95,	−0.38;	0.2974,	65.119,	0,	689.60,	−0.21;
0.2883,	46.435,	0,	676.95,	+0.18;	0.2839,	37.612,	0,	668.87,	+0.61;
0,2802,	30.088,	0,	660.08,	+1.30;					

Titration 3. $E_0(3) = 394.45 \pm 0.07$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.2912,	38.433,	0,	669.64,	−0.60;	0.2876,	43.693,	0,	674.33,	−0.34;
0.2851,	47.371,	0,	677.27,	−0.14;	0.2802,	54.537,	0,	682.80,	−0.17;
0.2754,	61.477,	0,	687.46,	−0.11;	0.2686,	71.416,	0,	693.42,	−0.11;
0.2621,	80.889,	0,	698.44,	−0.13;	0.2558,	90.092,	0,	702.68,	0.00;
0.2500,	98.525,	0,	706.40,	−0.05;	0.2404,	112.545,	0,	711.80,	+0.07;
0.2321,	124.559,	0,	716.05,	+0.09;	0.2183,	144.788,	0,	722.39,	+0.20;
0.2090,	158.294,	0,	726.40,	+0.11;	0.1987,	173.309,	0,	730.24,	+0.32;
0.1904,	185.426,	0,	733.35,	+0.30;	0.1806,	199.768,	0,	736.58,	+0.55;

Titration 4. $E_0(4) = 393.43 \pm 0.11$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.1752,	177.966,	0,	732.66,	−0.33;	0.1689,	151.823,	0,	726.90,	−0.05;
0.1609,	119.112,	0,	718.45,	−0.08;	0.1551,	95.184,	0,	710.20,	+0.24;
0.1477,	65.119,	0,	696.65,	+0.22;					

Titration 5. $E_0(5) = 428.68 \pm 0.09$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.1103,	23.888,	0,	698.70,	+0.38;	0.1061,	40.555,	0,	718.97,	−0.08;
0.1011,	60.391,	0,	734.45,	−0.18;	0.0938,	89.613,	0,	750.10,	−0.13;
0.0831,	132.280,	0,	766.10,	+0.02;					

Titration 6. $E_0(6) = 428.80 \pm 0.07$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.1154,	11.293,	0,	671.87,	+0.25;	0.1107,	22.467,	0,	696.90,	+0.04;
0.1080,	33.022,	0,	711.28,	−0.04;	0.0994,	67.273,	0,	738.92,	−0.30;
0.0903,	103.520,	0,	755.92,	+0.06;	0.0831,	132.280,	0,	766.24,	0.00;

Titration 7. $E_0(7) = 428.79 \pm 0.07$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.1143,	7.959,	0,	659.50,	−0.21;	0.1124,	15.609,	0,	682.93,	−0.20;
0.1101,	24.755,	0,	699.65,	−0.18;	0.1078,	33.614,	0,	710.99,	−0.11;
0.1053,	43.571,	0,	720.73,	−0.01;	0.1020,	56.886,	0,	731.18,	−0.17;
0.0986,	70.585,	0,	739.64,	−0.15;	0.0932,	91.729,	0,	750.00,	+0.01;
0.0905,	102.650,	0,	754.41,	+0.19;	0.0874,	114.84,	0,	758.94,	+0.31;
0.0831,	132.28 ,	0,	764.70,	+0.50;					

Titration 8. $E_0(8) = 429.36 \pm 0.04$; B,A,C,E, $(E_{calc}-E_{obs})$;

0.155,	26.957,	0,	699.20,	+0.38;	0.155,	40.144,	0,	714.02,	+0.17;
0.155,	53.054,	0,	724.42,	+0.11;	0.155,	64.693,	0,	731.92,	0.00;
0.155,	75.062,	0,	737.55,	−0.07;	0.155,	84.311,	0,	741.95,	−0.12;
0.155,	93.846,	0,	745.87,	−0.03;	0.155,	99.960,	0,	748.33,	−0.12;

0.1476, 103.626, 3.664, 748.95, −0.10; 0.1375, 108.640, 8.676, 749.78, −0.01;
0.1298, 112.465, 12.498, 750.67, −0.15; 0.1238, 115.421, 15.453, 751.25, −0.12;
0.1180, 118.285, 18.316, 751.66, +0.10; 0.1117, 121.407, 21.436, 752.31, +0.16;
0.1077, 123.420, 23.448, 753.13, −0.19; 0.1018, 126.313, 26.339, 753.67, 0.00;

Titration 9. $E_0(9) = 429.94 \pm 0.05$; B,A,C,E, $(E_{calc}-E_{obs})$;
0.6176, 68.075, 0, 716.00, −0.10; 0.6176, 100.19, 0, 731.07, −0.46;
0.6176, 165.00, 0, 749.75, −0.23; 0.6176, 244.05, 0, 764.34, −0.08;
0.6176, 304.41, 0, 772.51, +0.02; 0.6176, 337.50, 0, 776.45, −0.08;
0.6176, 384.85, 0, 781.25, −0.02; 0.6176, 420.51, 0, 784.39, +0.11;
0.6176, 460.68, 0, 787.60, +0.26; 0.6176, 499.89, 0, 790.66, +0.18;
0.6176, 504.89, 5.00, 790.67, +0.17; 0.6176, 509.79, 9.90, 790.65, +0.19;
0.6176, 517.83, 17.94, 790.70, +0.14; 0.6176, 526.23, 26.33, 790.75, +0.10;
0.6176, 530.68, 30.78, 790.77, +0.08; 0.6176, 538.41, 38.50, 790.72, +0.13;
0.6176, 549.90, 30.78, 790.80, +0.05; 0.6176, 502.16, 49.99, 787.05, +0.12;
0.6176, 466.47, 49.99, 784.17, −0.02; 0.6176, 430.99, 49.99, 780.95, −0.09;
0.6176, 382.35, 49.99, 775.95, −0.15; 0.6176, 305.80, 49.99, 766.35, −0.32;
0.6176, 244.17, 49.99, 755.40, −0.32; 0.6176, 173.26, 49.99, 738.80, −0.32;
0.6176, 130.26, 49.99, 721.55, +0.63;

Titration 10. $E_0(10) = 430.03 \pm 0.06$; B,A,C,E, $(E_{calc}-E_{obs})$;
0.6176, 82.93, 0, 723.80, −0.29; 0.6176, 157.75, 0, 748.40, −0.49;
0.6176, 296.86, 0, 771.75, −0.07; 0.6176, 384.61, 0, 781.15, +0.15;
0.6176, 499.89, 0, 790.46, +0.48; 0.6176, 510.88, 10.98, 790.47, +0.47;
0.6176, 529.75, 29.85, 790.53, +0.41; 0.6176, 549.90, 49.99, 790.65, +0.29;
0.6176, 519.08, 49.99, 788.40, +0.21; 0.6176, 482.55, 49.99, 785.53, +0.10;
0.6176, 440.86, 49.99, 781.90, 0.00; 0.6176, 387.66, 49.99, 776.51, −0.03;
0.6176, 341.38, 49.99, 771.13, −0.14; 0.6176, 296.68, 49.99, 765.00, −0.24;
0.6176, 234.59, 49.99, 754.16, −0.31; 0.6176, 217.25, 49.99, 750.25, −0.12;
0.6176, 200.30, 49.99, 746.30, −0.21; 0.6176, 160.10, 49.99, 734.48, −0.20;

$10^{-7} \times \beta_2 = 5.713 \pm 0.240$ $(= \sigma(\beta_2))$; $\log \beta_2 = 7.757 \pm 0.018$
$10^{-9} \times \beta_3 = 9.0564 \pm 0.0526$ $(= \sigma(\beta_3))$; $\log \beta_3 = 9.957 \pm 0.003$
$\sigma(E) = \pm 0.38$ mV

In the calculation the seven first titrations in Table 1 were used.

In 3.0 M $Na(ClO_4)$ Carell and Olin obtained the following equilibrium constants: $\log \beta_2 = 10.9 \pm 0.1$, $\log \beta_3 = 13.66 \pm 0.05$. If we compare these constants with the constants of the present work we find that the complex formation between Pb^{2+} and OH^- seems to be weaker in 3.0 M Na(Cl) than in 3.0 M $Na(ClO_4)$. That would indicate a stronger complex formation between Pb^{2+} and the medium ions in 3.0 M Na(Cl) than in 3.0 M $Na(ClO_4)$.

Determination of $[OH^-]$ *in alkaline borate solutions by using a lead amalgam electrode.* In strongly alkaline solution $[Pb^{2+}]$ may be neglected compared with $[Pb(OH)_2]$ and $[Pb(OH)_3^-]$ and eqn. (5a) is in that case reduced to $B = \beta_2 ba^2 + \beta_3 ba^3$. Eliminating b from this expression and inserting in (3) gives

$$E = E_0 + 29.578 \log \beta_3 + 3 \times 29.578 \log a - 29.578 \log B + 29.578 \log (1 + \beta_2\beta_3^{-1}a^{-1}) + E_j \quad (12)$$

For the correction term $E_{corr} = 29.578 \log (1 + \beta_2\beta_3^{-1}a^{-1})$ due to formation of $Pb(OH)_2$ the following values may be calculated:

$[OH^-]$ M	1.00	0.50	0.40	0.30	0.20	0.10	0.05	0.04	0.03	0.02	0.01
E_{corr} mV	0.07	0.16	0.21	0.28	0.41	0.83	1.57	1.99	2.57	3.67	6.52

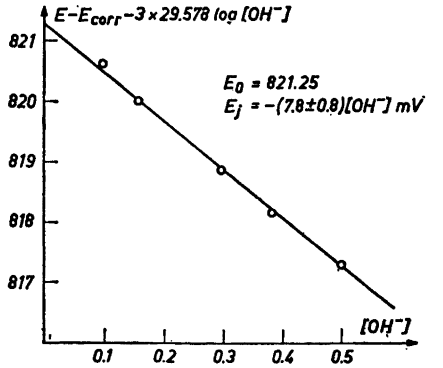

Fig. 3. Result of an amalgam electrode $[OH^-]$-calibration.

Graphical $[OH^-]$*-determination.* Before titrating a borate solution with unknown $[OH^-]$ the lead amalgam electrode was calibrated by titrating in solutions without borate and with known amounts of $[OH^-]$ and B. $[OH^-]$ was calculated from the relation, $[OH^-] = A - 3B$. In a diagram where $(E - E_{corr} - 3 \times 29.578 \log [OH^-])$ was plotted against $[OH^-]$ the quantity $(E_0 + E_j)$ at different $[OH^-]$ was obtained. A result from such a calibration is given in Fig. 3. In a titration where $[OH^-]$ is unknown it is possible from the measured emf and the calibration curve to calculate $[OH^-]$ (by using eqn. (12)). In the borate solutions investigated it was found, that within the accuracy of the emf-measurement only one OH^- is bound per $B(OH)_3$. It means that the borate species present is $B(OH)_4^-$ and in the $[OH^-]$-range investigated, 0.070—0.500 M, there are no indications for formation of, for instance, $H_2BO_3^{2-}$ or BO_3^{3-}. Note that titrations 9 and 10 (Table 1) also contain back-titrations.

The result from the titrations is visualized in Figs. 4a and 4b. In 4a the average charge per boron Y, is plotted against the total boron concentration, C, and Fig. 4b gives Y as a function of $[OH^-]$. The dotted upper and lower

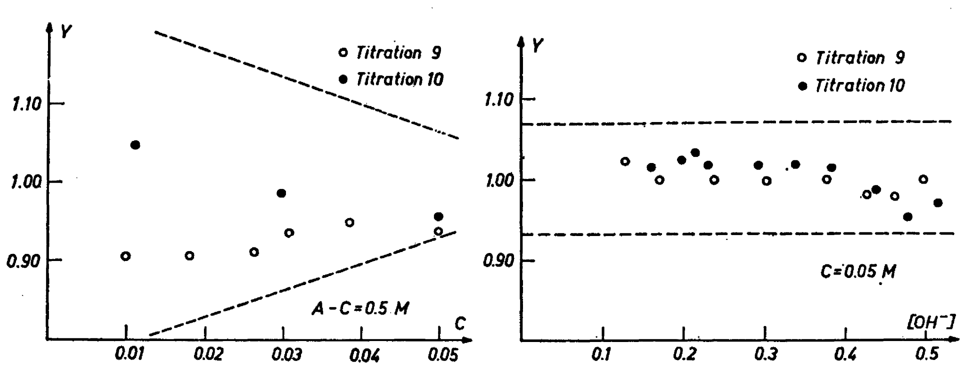

Fig. 4. Result of titrations 9 and 10 (back-titrations). The average charge per boron, Y, a) as a function of the total boron concentration C, and b) as a function of $[OH^-]$.

lines in the diagrams give the limits within which the points would be expected if we assume an accuracy in the emf-measurement of $\pm$ 0.3 mV.

Computer calculations. In a final computer calculation we used both data from the titrations with and without boron and determined the best values of β_2, β_3, and E_0. In this calculation we assumed all boron to be in the form $B(OH)_4^-$. This calculation showed no greater systematical deviations for the titrations with boron than for the titrations without boron. It means that $B(OH)_4^-$ is the main species in the solutions investigated. The calculation gave the following equilibrium constants and standard deviations.

$10^{-7} \times \beta_2 = 6.061 \pm 0.156$ $(= \sigma(\beta_2))$; $\log \beta_2 = 7.783 \pm 0.011$
$10^{-9} \times \beta_3 = 9.1711 \pm 0.0256$ $(= \sigma(\beta_3))$; $\log \beta_3 = 9.962 \pm 0.001$
$\sigma(E) = \pm 0.28$

The variation of the E_0-values gave the following best values and standard variations; the differences reflect different composition of the amalgam in different experiments.

$E_0(1) = 396.36 \pm 0.05$	$E_0(6) = 428.80 \pm 0.07$
$E_0(2) = 397.14 \pm 0.29$	$E_0(7) = 428.79 \pm 0.07$
$E_0(3) = 394.45 \pm 0.07$	$E_0(8) = 429.36 \pm 0.04$
$E_0(4) = 393.43 \pm 0.11$	$E_0(9) = 429.94 \pm 0.05$
$E_0(5) = 428.68 \pm 0.09$	$E_0(10) = 430.03 \pm 0.06$

In Table 1 the differences, $E_{calc}-E_{obs}$, are given for every point. E_{calc} is the emf value calculated with the constant given above and E_{obs} the experimental emf value. For the liquid junction potential we found the relation $E_j = -4.0 \times [OH^-]$ mV, by special experiments (*cf.* Ref. 3).

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