

Supplemental Information to accompany:

Phenyl boronic acid complexes of diols and hydroxyacids.

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Contents

Experimental details for potentiometric titrations.

Structure of the data archive

Structure of the data files

Potentiometric titrations

Solutions were prepared volumetrically using degassed deionized and distilled water and HPLC grade methanol. Stock solutions were prepared from the solids obtained commercially in > 99% purity. Nitric acid titrant, diluted from concentrated HNO₃, was standardized bi-weekly *versus* sodium borate. Sodium hydroxide was prepared weekly and standardized against the primary standard, potassium hydrogen phthalate (phenolphthalein endpoint), and by direct titration with the secondary standard HNO₃ as titrant.

The titrations were performed using a Mettler DL21 automatic titrimer with data collection to a custom macro running under Microsoft Excel. The macro controlled the functions of the titrimer via a serial port to the automatic titrimer. The titrations were performed in a closed jacketed cell at a temperature of 25.0 ± 0.2 °C under an atmosphere of nitrogen. The measurement circuit consider of: glass electrode | titration solution | glass frit | 0.1 M NaNO₃ in water or 0.1M NaNO₃ in 1:2 MeOH:water | glass frit | saturated KCl in water | AgCl/Ag. The system was designed to allow titration of 4.0 mL of solution. The electrode system was calibrated daily, according to the protocol outlined for the program GLEE¹ modified for the acid-into-base titration mode. Thus, electrolyte (0.1M NaNO₃ in water or 0.1 M NaNO₃ in 2:1 M:W, 4.0 mL) and a known amount of sodium hydroxide was titrated with HNO₃, and the resultant strong acid - strong base curve of potential *versus* volume was converted via the standard concentrations to a curve of potential *versus* p[H⁺]. The required pK_w value for 0.1M NaNO₃ in water was taken from Martell² (13.78). The pK_w value in 0.1M NaNO₃ in 1:2 M:W (13.82) was determined by the procedure of Jameson and Wilson³ using the pH meter calibrated using buffers prepared in 33.3 wt% methanol.⁴ The curve of potential *versus* p[H⁺] was linear between $2.4 < \text{p[H}^+] < 11.4$ in both solvent systems, and gave a slope of >99% of the Nernstian value and an intercept value for the electrode. Triplicate values of the slope and intercept were determined daily for use in calculation of the formation constants determined that day. The intercept value over time (weeks) was constant ± 1.6 mV, taken as the standard error. The standard error in the titer was determined from a series of gravimetric experiments to be 0.0002 ml for an aliquot volume of 0.01 ml, using the 1.0 ml buret on the titrimer.

Solutions for titration were prepared from stock solutions of the using microliter syringes and calibrated 5.0 ml volumetric flasks. Solutions in methanol water utilized methanolic stock solutions of the boronic acids, plus additional methanol as required, made to the final volume with water. All solutions included a sufficient volume of standard sodium hydroxide to fully deprotonate the boronic acid, plus the other acids if present. A 4.0 ml sample was titrated within 2 hours of solution preparation. Duplicate solutions prepared independently from the same stock solutions were routinely prepared. Each system involved at least two, and usually three different concentrations (relative stoichiometries) of the components. Concentrations and aliquot volumes were chosen to produce 30-70 significant data points from each titration to give 90 – 140 points per system including duplicates/triplicates.

The titrimeter macro exported a formatted file for direct input to HYPERQUAD.⁵ For each system, the individual titration curves were examined to explore the possible complexes to be considered, followed by a final computation involving one curve at each composition. The duplicate data were then computed using the same model. The refined parameters differed by less than the computed standard deviations in all cases of direct duplicates prepared from a common stock solution. HYPERQUAD produces a goodness-of-fit statistic (chi-squared) that indicates if the residuals (calculated – experimental) are normally distributed relative to a determined measurement precision.⁵ The only species included in the input model were those required to generate a chi-squared value better than that expected for the 95% confidence level. On a practical level this means that the species usually must account for >20% of the total boronic acid concentration for some range of data in the titration curve. A preliminary survey allowed a choice of concentrations and stoichiometric ratios to ensure that the minor species fulfilled this requirement. The overall reliability of the data was determined by comparison of independently prepared replicates as discussed in the text.

HYPERQUAD files for each of the systems (boronic acid plus diol or hydroxyacid) reported are deposited in a data archive with one folder for each system. The archive is divided into directories for titrations in water and in methanol-water, and within those directories by system. Within each system folder are three HYPERQUAD files. Files with a *.con extension describe the file locations of a HYPERQUAD project. Files with a *.par extension describe the identities and stoichiometries of the species considered and how the program should treat the given values of the cumulative formation constants given (hold constant, refine, ignore). Files with a *.ppd extension present the individual titration curves, giving concentrations of the species in the cell and the titrant, the electrode calibration data, and the recorded data pairs. Each *.ppd contains three or more independent titration curves. The files will execute directly with HYPERQUAD.

The data files are structured as given below.

Sample *.par file (~MW/PBA/PBA.par)

```
phenylboronic acid      (title)
 25      0 6 0 0 2 4 0 4 0 0 0 2 2 2 0 0
H        0              (species identities)
Pba      0
25.0000    0.3300      (temperature; standard error)
 8.8000    1      1      1 1(log beta, h and b stoichiometry, refine)
-13.7800   -1      0      0 0
```

Sample *.ppd file (~MW/PBA/PBA.ppd)

```
pba1b      (curve title)
0 1-3.000E-03 2.780E-01 1 0 (cell (mmol) and titrant conc (M) for H)
0 2 6.000E-03 0.000E+00 0 0 (cell (mmol) and titrant conc (M) for PBA)

0 4.000000 0.000200      (cell volume in ml, volume error)
0 1 1 391.4000 1.5000 0 0.9870 (electrode E0, error, slope factor)

0.002000 -222.1000      1 (volume added in ml, cell potential)
```

0.004000	-216.2000	1
0.006000	-207.2000	1
0.008000	-194.1000	0
0.010000	-178.4000	0
0.012000	-162.8000	0
0.014000	-149.9000	0
0.016000	-139.0000	0
0.018000	-128.9000	0
0.020000	-118.7000	0
0.022000	-108.8000	0
0.024000	-97.7000	0
0.026000	-83.5000	0
0.028000	-64.4000	0
0.030000	-30.1000	0
0.032000	141.9000	1
0.034000	185.0000	1
0.036000	198.1000	1
0.038000	206.6000	1
0.040000	213.1000	1
0.042000	218.3000	1
0.044000	222.5000	1
0.046000	226.3000	1

pba1a (next curve title)

0	1	-3.000E-03	2.780E-01	1	0
0	2	6.000E-03	0.000E+00	0	0
0	4	0.000000	0.000200		
0	1	1	391.4000	1.5000	0
					0.9870

0.002000	-224.6000	1
0.004000	-220.2000	1
0.006000	-213.1000	1
0.008000	-201.3000	0

(etc.)

References

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- (5) Sabatini, A.; Vacca, A.; Gans, P. *Talanta* **1996**, *43*, 53-65.