Aryl Phosphate Complexation by Cationic Cyclodextrins. An Enthalpic Advantage for Guanidinium over Ammonium and Unusual Enthalpy-Entropy Compensation.

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Supporting Information

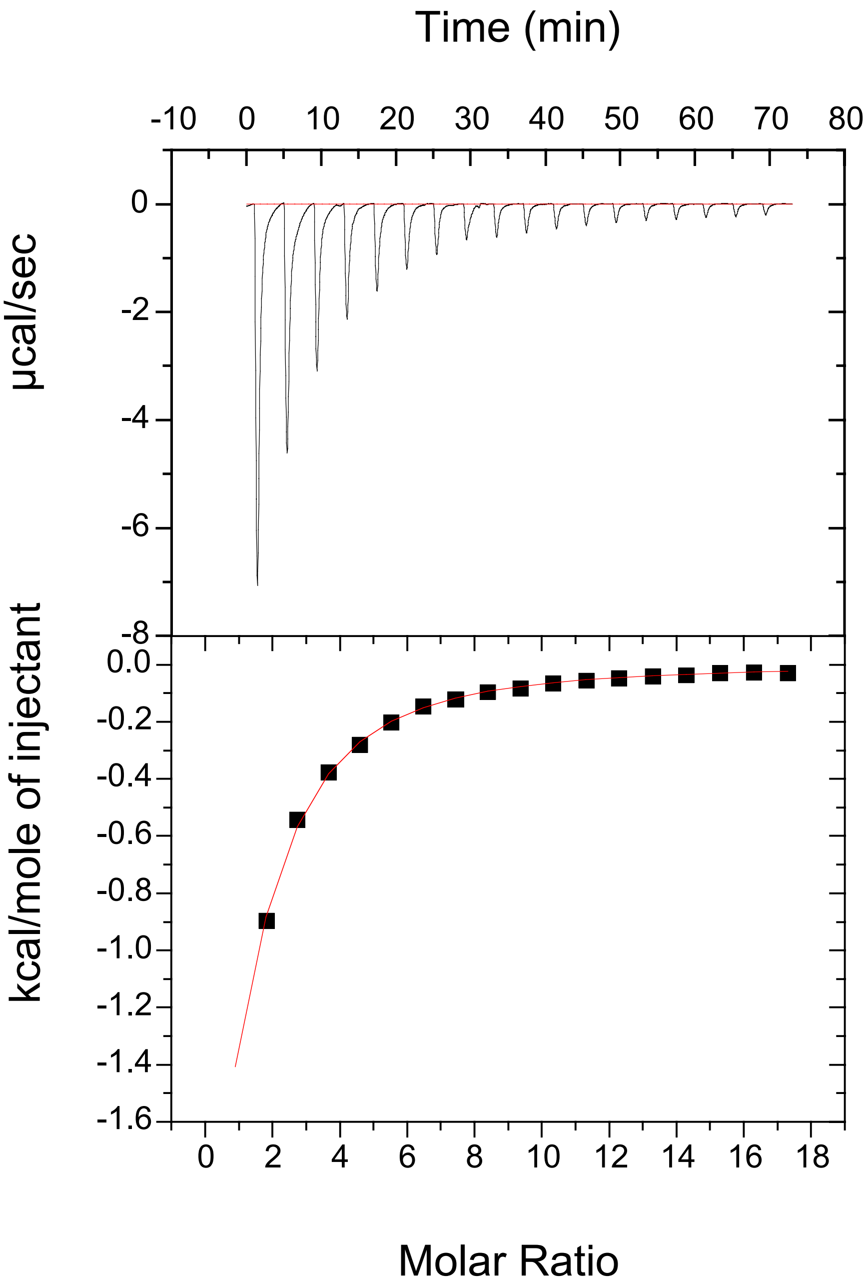
Experimental Details for Calorimetry Experiments.

Experiments were conducted using a MicroCal VP-ITC instrument and all data were analyzed using the software provided by MicroCal. Guest solutions were prepared by dissolving the appropriate amount of aryl phosphate in phosphate buffer (pH 7.00) and deionized water such that the total phosphate concentration was equal to 100 mM after adjustment of the pH to 7.00 with aqueous sodium hydroxide. The approximate guest concentrations for titrations were 50 mM for phenyl phosphate and phosphotyrosine and 25 mM for diamides **7** and **8**. The calorimeter cell (1.7 mL) was filled with a solution of host (ca. 200 µM in 100 mM phosphate buffer, pH 7.00). After equilibration of the cell to 25.0 °C, 180 µL of guest was added in individual 10 µL injections. The resulting data was used to obtain enthalpies and association constants after subtraction of the heat of dilution for the guest (obtained from a titration in which the cell contained 100 mM phosphate buffer but no host).

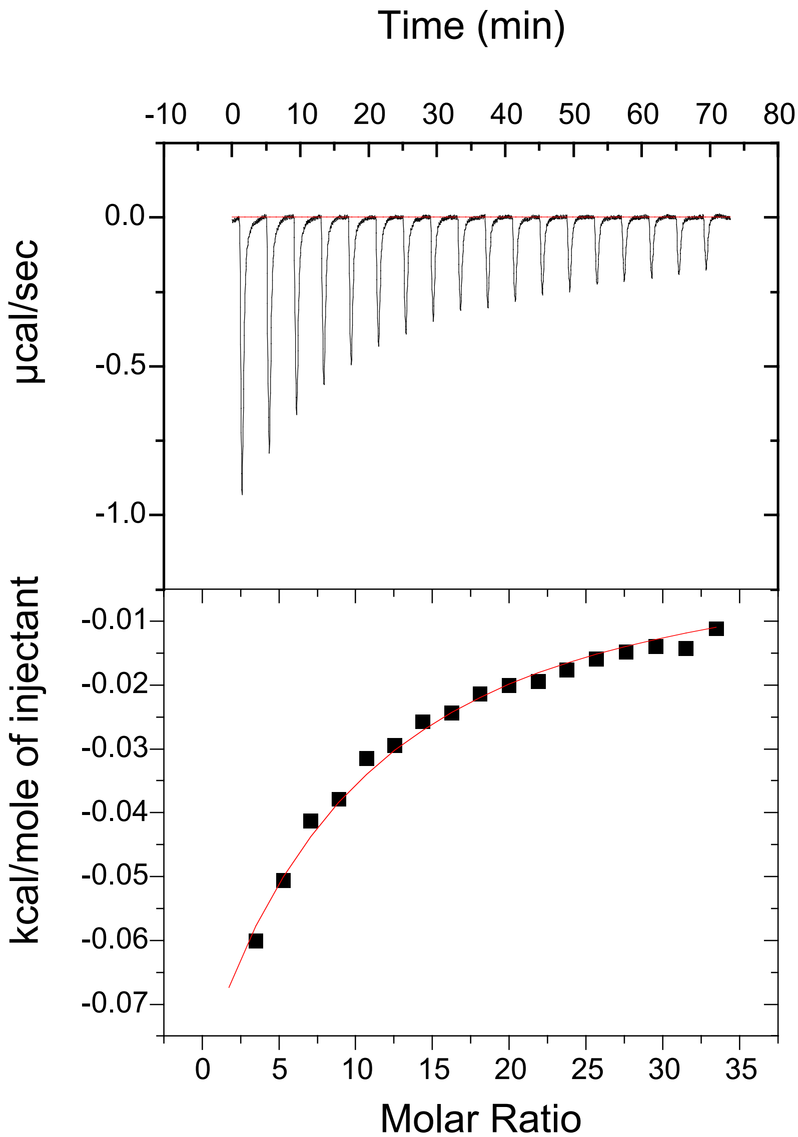
Two examples of primary data and the resulting curve fits are provided on the following pages. (The upper panel shows the heat evolved for each injection, uncorrected for the heat of dilution for the guest; the lower panel shows the fit of the data to a simple 1:1 binding model after subtraction of the heat of dilution for the guest.)

A. Strong binding/large negative heat of complexation. Binding of host **4** with guest **7**.

B. Weak binding/small negative heat of complexation. Binding of host **2** with guest **6**.



A. Data for binding of host **4** with guest **7**.



B. Data for binding of host **2** with guest **6**.