Supporting Information for:

Effects of crowding by Mono-, Di-, and Tetra-Saccharides on Cytochrome c - Cytochrome c Peroxidase Binding: Comparing Experiment to Theory

Artemiza S. Morar, Xuming Wang and Gary J. Pielak*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

*To whom correspondence should be addressed.
Phone: (919) 966-3671. Fax: (919) 966-3675.
E-mail: gary_pielak@email.unc.edu
Modified Scaled-particle Theory

Using Berg's terminology (1), the free energy for creating hard spherical cavities or hard spherical dimers in a solution of hard spheres is given by eq. 1

\[
g(r_b, \Phi) = -\ln(1-S_3) + \left[ \frac{6RS_2}{(1-S_3)} \right] r_2 + \left[ \frac{12SS_1}{(1-S_3)} + \frac{18S_2^2}{(1-S_3)^2} \right] r_b^2 \tag{1}
\]

where all the symbols except \( R, S, \) and \( T \) are described in the original reference. For a spherical cavity of radius \( r_a \), \( R, S \) and \( T \) are unity and eq. 1 is equivalent to Berg's eq. A1. For a hard dimer made from spheres of diameter \( r_a \) and \( r_b \),

\[
R = 1 + L(p+1) + \frac{1}{4L} \frac{(p-1)^2}{(p+1)} \tag{2}
\]

\[
S = \frac{1}{2} (p^2 + 1) + \frac{1}{4} L(p+1)^2 + \frac{1}{4L} (p-1)^2 \tag{3}
\]

\[
T = \left( \frac{1}{3} R^2 + \frac{2}{3} S \right) \tag{4}
\]

where \( p = r_a/r_b \) and \( L = 1/(r_a + r_b) \), where \( L \) is the distance between the centers of the spheres. Eq.s 2–4 were adapted from eq.s 48 and 51 of Boublík (2). When \( r_a = r_b \) the heterodimer becomes a homodimer and eq. 1 is equivalent to Berg's eq. A1.

The volume of a heteronuclear hard-sphere dimer made from spheres of radius \( r_a \) and \( r_b \) is
\[ V = \frac{2}{3} \pi \left[ p^3 + 1 + \frac{3}{4} \left( L(p+1) \right) \left( p^2 + 1 \right) \right] - \frac{1}{8} \left[ L^3 (p+1)^3 + \frac{3(p+1)(p-1)^2}{L} \right] r_b^3 \ldots \ldots 5 \]

Eq. 5 is defined for \( L < (p-1)/(p+1) \). When \( L \leq (p-1)/(p+1) \) the heterodimer collapses to a sphere of radius \( r_a \) or \( r_b \), whichever is smaller. (Note that eq. 51 in Boublík is not quite correct; the leading fraction should be \( 1/12 \).)

We used Berg's method (1) to maintain constant pressure (his eqs A9a and A9b). This method allows cavity formation free energies to be calculated for cosolutes lacking measured solution densities. As we have shown (3), using this method instead of the measured densities, does not alter the conclusions. We validated eq.s 1-5 by reproducing Fig. 6 in Berg's paper.

