Study on the supramolecular interaction of astemizole with cucurbit[7]uril and its analytical application

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Supplementary Information

Content Page

Derivation of Eq. 1

The association constant ($K_{\text{CB[7]-AST}}$) was determined with the competitive binding method.[1-4] We first consider a systerm in which the indicator PAL and the substrate AST form only 1:1 complexes with the host CB[7]. The competitive complexation equilibrium is

CB[7]-PAL +AST $\Leftrightarrow$ CB[7]-AST + PAL (S-1)

The systems involve two independent equilibria (Eq. (S-2) and (S-3)), two binding constant expressions (Eq. (S-4) and (S-5)), and three mass balance equations (Eq. (S-6)–(S-8)).

CB[7] + PAL $\Leftrightarrow$ CB[7]-PAL (S-2)

CB[7] + AST $\Leftrightarrow$ CB[7]-AST (S-3)

$K_{\text{CB[7]-PAL}}$ = [CB[7]-PAL]/([CB[7]][PAL]) (S-4)

$K_{\text{CB[7]-AST}}$ = [CB[7]-AST]/([CB[7]][AST]) (S-5)

$[\text{CB[7]}]_t$ = [CB[7]] + [CB[7]-PAL] + [CB[7]-AST] (S-6)

$[\text{PAL}]_t$ = [PAL] + [CB[7]-PAL] (S-7)

$[\text{AST}]_t$ = [AST] + [CB[7]-AST] (S-8)

We use these equations as a starting point to derive an equation involving only one unknown concentration, and in this case we chose [CB[7]]. We therefore focus on Eq. (S-6) and seek to define all other concentrations in terms of [CB[7]]. Accordingly, combining Eq. (S-4)–(S-8) yields Eq. (S-9)–(S-11).

$$[CB[7]-AST]=\frac{K_{CB[7]-AST}[CB[7]]}{1+K_{CB[7]-AST}[CB[7]]}[AST]_t \qquad \text{(S-9)}$$

$$[CB[7]-PAL]=\frac{K_{CB[7]-PAL}[CB[7]]}{1+K_{CB[7]-PAL}[CB[7]]}[PAL]_t \qquad \text{(S-10)}$$

$$[PAL]=\frac{[PAL]_t}{1+K_{CB[7]-PAL}[CB[7]]} \qquad \text{(S-11)}$$

Substituting Eq. (S-9) and (S-10) into Eq. (S-6) in turn leads to Eq. (S-12).

$$[CB[7]]_t = [CB[7]] + \frac{K_{CB[7]-AST}[CB[7]]}{1+K_{CB[7]-AST}[CB[7]]}[AST]_t + \frac{K_{CB[7]-PAL}[CB[7]]}{1+K_{CB[7]-PAL}[CB[7]]}[PAL]_t \qquad \text{(S-12)}$$

Defining Q = [PAL]/[CB[7]-PAL] allows us to write $K_{\mathrm{CB[7]\text{-}PAL}} = 1/Q$[CB[7]], which, substituted into Eq. (S-12), gives

$$[CB[7]]_t = \frac{1}{QK_{CB[7]-PAL}} + \frac{[AST]_t K_{CB[7]-AST}}{QK_{CB[7]-PAL} + K_{CB[7]-AST}} + \frac{[PAL]_t}{Q+1} \qquad \text{(S-13)}$$

The quantity P is defined as

$$P = [CB[7]]_t - \frac{1}{QK_{CB[7]-PAL}} - \frac{[PAL]_t}{Q+1} \qquad \text{(S-14)}$$

Therefore Eq. (S-13) may be written

$$P = \frac{[AST]_t K_{CB[7]-AST}}{QK_{CB[7]-PAL} + K_{CB[7]-AST}}$$

or

$$\frac{[AST]_t}{P} = \frac{K_{CB[7]-PAL}}{K_{CB[7]-AST}}Q + 1 \qquad \text{(S-15)}$$

The Q can be obtained from Eq. (S-16),[1,2]

$$Q = \frac{F - F_\infty}{F_0 - F} \qquad \text{(S-16)}$$

Where $[\mathrm{CB[7]}]_t$ is initial concentration of CB[7].

$[\mathrm{PAL}]_t$ is initial concentration of PAL.

$[\mathrm{AST}]_t$ is concentration of AST.

$K_{\mathrm{CB[7]\text{-}PAL}}$ is the association constant between CB[7] and PAL.

$K_{\mathrm{CB[7]\text{-}AST}}$ is the association constant between CB[7] and AST.

F_0 and F_∞ is the fluorescence intensity of the sample solution when the PAL is completely converted to the free and complexed form, respectively.

F is the fluorescence intensity of the sample solution when AST was titrated into it.

Determination of association constant between CB[7] and AST ($K_{CB[7]-AST}$)

A 1.0 mL solution of 10 μM CB[7] was poured into a 10 mL colorimetric flask, to which 1.0 mL of the 10 μM PAL solution and 1.0 mL of 0.001 M hydrochloric acid were also added. Suitable amounts of AST solution were then sequentially added to the flask. The mixture was diluted to volume with double-distilled water and shaken for 5 min at room temperature. The fluorescence intensity were measured at 495 nm using an excitation wavelength of 343 nm. Then, the fluorescence intensity of the free PAL solution (1.0 μM) and the completely complexed PAL solution (1.0 μM PAL with 4.0 μM CB[7]) were measured in the same experimental conditions. The association constant between CB[7] and AST was estimated using Eq. (S-15) by ploting [AST_t /P to Q. The association constant ($K_{CB[7]-AST}$) can been obtained from the slope and the known $K_{CB[7]-PAL}$.[5]

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