

## The cooperative effect of the third component on the isotherms of guest vapour inclusion in solid *tert*-butylcalix[4]arene

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The observed sigmoidal isotherms of guest vapour sorption on solid *tert*-butylcalix[4]arene may be transformed to Langmuir or BET isotherms in the presence of small concentrations of a third component.

The binding properties of cavitands in solution and in the solid phase are known to be fundamentally different. Some host–guest complexes are exceedingly stable in the solid phase but are not formed in the solution.<sup>1,2</sup> The threshold of the guest concentration necessary for its inclusion in the host was observed for several solid<sup>3–5</sup> or liquid crystalline<sup>6</sup> host–guest complexes. These facts indicate that unlike solutions the host–guest interaction in the solid phase can be cooperative. However, only qualitative information about the cooperative influence of the third component on the stoichiometry of solid inclusion complexes<sup>7</sup> and their decomposition<sup>8</sup> is available at present.

The aim of the present work is to investigate the effect of the small concentrations of the third component on the sorption isotherms for vapour guest–solid *tert*-butylcalix[4]arene **1** systems. The vapour sorption isotherms of guests with different molecular structures (benzene, toluene, acetonitrile, ethanol) on solid **1** in binary systems and in the presence of a third component (isooctane = 2,2,4-trimethylpentane, toluene, acetonitrile, ethanol) were determined by the method of static headspace gas chromatographic analysis.

The cavitand **1** was synthesized as described in ref. 9, and purified from volatile impurities by heating at 190–210 °C during 3–4 h *in vacuo* (100 Pa). The absence of volatile compounds was tested by the displacement method: 3–5 mol% of methanol were added to **1** and then the vapour phase was analysed after equilibration. Purified samples of cavitand **1** with different amounts of studied guests were maintained for 100 h at 298 K in hermetically closed vials. The thermodynamic activity of sorbate ( $a = P/P_0$ ) was then determined for each sample at 298 K as a ratio of the partial vapour pressure  $P$  and the saturation vapour pressure  $P_0$  of the sorbate in the studied system and in the pure liquid state, respectively. The sorbed quantity of guest was calculated as the difference between the added sorbate quantity and its amount in the vapour phase. After each experiment the solid samples were treated as mentioned above to expel the guest molecules and the determination of the sorption isotherm was performed once more. The sorption isotherms in these subsequent experiments did not differ within experimental errors. The accuracy of

sorbate activity determination is in the interval from 5% (for  $P/P_0 > 0.5$ ) to 10% (for  $P/P_0 < 0.1$ ). The concentration  $X$  of the third component in mol/mol of host **1** was made constant for each studied isotherm in the ternary systems. The headspace sampler of original construction for capillary gas chromatography was described earlier.<sup>10</sup>

The sorption isotherms obtained are presented in Figure 1. Monolayer (Langmuir) or multilayer (BET)<sup>11</sup> sorption models can not be used for an approximation of the isotherms for the binary systems studied. One can see (Figure 1) that there is a threshold of guest activity necessary for its incorporation in solid cavitand on these isotherms. Up to this activity  $a_{\text{thr}}$  (Table 1) practically no binding of the guests by solid **1** is observed, whereas above  $a_{\text{thr}}$  the guest sorption rises enormously. The phase transition between two crystalline phases was proposed earlier for an explanation of the concentration threshold in guest sorption kinetics on a solid host.<sup>6</sup>

Since most of the isotherms obtained have a sigmoidal shape, we applied for their approximation the Hill equation (1)<sup>12</sup> used in a generalized form for the description of the cooperative behaviour of biological systems.<sup>13</sup>

$$YS = \frac{SC(P/P_0)^N}{1 + C(P/P_0)^N} \quad (1)$$

In equation (1)  $Y$  is the complex saturation extent,  $S$  is the stoichiometry,  $C$  is the sorption constant,  $N$  is the cooperativity constant and  $YS$  the solid phase composition (mol of guest per mol of host). The stoichiometry  $S$  was estimated by the experimental  $YS$  value of the saturation parts of the isotherms. The cooperativity constant  $N$  and the sorption constant  $C$  were calculated for the linear part of the isotherms in coordinates  $\ln[Y/(1-Y)]$  vs.  $\ln(P/P_0)$  by equation (2) derived from equation (1):

$$\ln \frac{Y}{1-Y} = \ln C + N \ln \frac{P}{P_0} \quad (2)$$

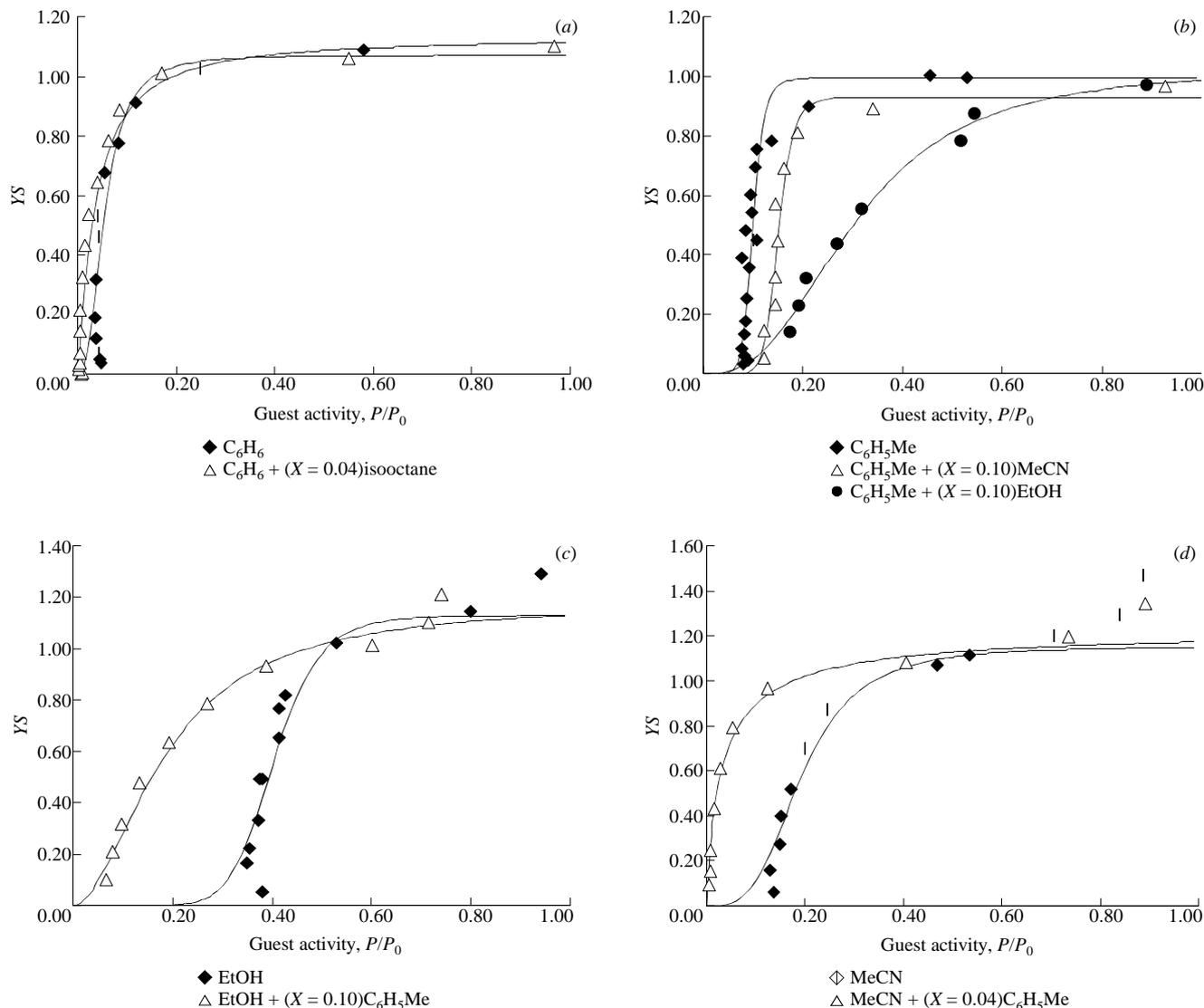
Calculated parameters  $N$  and  $C$  and the  $Y$  interval used for their calculation are given in Table 1. As can be seen from

**Table 1** Parameters for the sorption isotherms of vapour guests on solid *tert*-butylcalix[4]arene for binary systems and in the presence of a constant concentration of a third component at 298 K.

Guest + (X)mol of a third component per mol of the host	$a_{\text{thr}}$	$S^a$	$\Delta Y^b$	$N^c$	$\ln C^c$	$\delta^d$
MeCN	0.13	1.15	0.14–0.97	3.3±0.3	5.5±0.4	0.02
MeCN + (0.04)C <sub>6</sub> H <sub>5</sub> Me	0.006	1.24	0.20–0.78	0.8±0.1	2.9±0.2	0.01
EtOH	0.36	1.13	0.15–0.91	8.9±0.9	8.0±0.8	0.02
EtOH + (0.10)C <sub>6</sub> H <sub>5</sub> Me	0.04	1.18	0.09–0.94	1.9±0.1	3.1±0.2	0.02
C <sub>6</sub> H <sub>6</sub>	0.04	1.07	0.11–0.85	2.6±0.5	7.4±1.6	0.01
C <sub>6</sub> H <sub>6</sub> + (0.04)isooctane	0.04	1.13	0.02–0.97	1.2±0.1	4.0±0.3	0.01
C <sub>6</sub> H <sub>5</sub> Me	0.08	0.99	0.03–0.76	8.9±2.4	20.4±5.8	0.01
C <sub>6</sub> H <sub>5</sub> Me + (0.10)MeCN	0.14	0.93	0.06–0.87	10.1±1.5	19.1±2.9	0.01
C <sub>6</sub> H <sub>5</sub> Me + (0.10)EtOH	0.19	1.03	0.14–0.94	2.7±0.1	3.2±0.2	0.02

<sup>a</sup>Estimation error of the stoichiometry  $S$  is ±5%. <sup>b</sup> $\Delta Y$  is the interval of  $Y$  for which  $N$  and  $C$  were calculated by equation (2). <sup>c</sup> $N$  and  $\ln C$  are shown with the standard errors. <sup>d</sup> $\delta$  is the standard deviation of the approximation in the interval  $\Delta Y$  for the shortest distances between experimental points and the calculated line:

$$\delta = \sqrt{\sum \{[(P/P_0)_{\text{calc}} - (P/P_0)_{\text{exp}}]^2 + [(YS)_{\text{calc}} - (YS)_{\text{exp}}]^2\} / (n-2)}$$



**Figure 1** Vapour sorption isotherms for various guests on solid *tert*-butylcalix[4]arene at 298 K in binary host–guest systems and in the presence of a constant concentration  $X$  (in mol per mol of host) of a third component.  $Y_S$  is the solid phase composition (mol of guest per mol of host). The solid lines correspond to the isotherms calculated by the Hill equation (1).

Figure 1 the Hill equation is a rather good model for the approximation of the isotherms obtained. For all systems studied the obtained stoichiometry of the host–guest complex is *ca.* 1:1. The 1:1 stoichiometry for complexes of benzene and toluene with **1** coincides with the available results of the X-ray method.<sup>14,15</sup> In the systems studied the third component has no effect on the stoichiometry of the host–guest complexes. At the same time even small concentrations of the third component compared to the concentration of the guest have a significant effect on the activity threshold and the shape of the isotherms. This fact allows us to consider the influence of the third component to be cooperative. As a result the sorption isotherms of benzene in the presence of small concentrations of isooctane, and isotherms of acetonitrile and ethanol in the presence of toluene, are transformed from sigmoidal to Langmuir or BET isotherms with  $a_{\text{thr}} \rightarrow 0$  and  $N \approx 1$  (Table 1). The absence of a threshold effect for the sorption of guest by thin layers (40 nm) of cavitated on an alkylsilylated quartz surface was observed for several vapour guest–solid host systems<sup>16–19</sup> including the system toluene–**1**.<sup>19</sup> This fact may be the result of the analogous cooperative influence of an alkylsilyl coating on the binding properties of the host thin layer studied by a quartz microbalance method.

In some systems (toluene + 0.10 mol acetonitrile per mol of the **1** and toluene + 0.10 mol ethanol per mol of the **1**) the effect of the third component has the opposite sign: the activity

threshold increases. The different relation between the sizes of the guest and the third component molecules and between their host binding energies in these systems may be a reason for the observed effect of the third component on the guest threshold activity.

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