Journal of Physical Chemistry B 2002 vol.106 N23, pages 5845-5851

Nonlinear structure - Affinity relationships for vapor guest inclusion by solid calixarenes

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Abstract

The structure-affinity relationships were studied for the guest inclusion parameters of solid tert-butylthiacalix-[4]arene (1) and tert-butylcalix[4]arene (2). The inclusion stoichiometry and inclusion free energy were calculated by the sorption isotherms obtained for guest vapor-solid host systems by the static method of headspace gas chromatographic analysis at 298 K. The obtained sorption isotherms have an inclusion threshold for guest thermodynamic activity corresponding to the phase transition between the initial host phase and the phase of inclusion compound. Unlike tert-butylcalix[4]arene, its thia analogue having a larger molecular bowl is able to bind only initial members of each studied homological series. All inclusion compounds of 1 formed upon host saturation by guest vapors have the same 1:1 stoichiometry, while for 2 the inclusion stoichiometry depends on the guest molecular size. A linear correlation between the inclusion free energy (standard state: infinitely dilute guest solution in toluene) and the guest size parameter (molar refraction) was observed for 1: ΔGtrans (kJ mol-1) = -12.24 + 0.568MRD (n = 7, r = 0.972, RSD = 0.6). This correlation is regarded as a part of the V-like structure-affinity relationship with a minimum for a guest that is complementary to the host cavity.

http://dx.doi.org/10.1021/jp014352j