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Using clathrate pseudopolymorphism for a single sensor detection of target component in the headspace of liquid mixture

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ABSTRACT

A new sensing mechanism for mass-sensitive sensors is offered, which is based not on the preferential binding as usual, but on the specific shape of sensor kinetic response. The used mechanism includes formation of an intermediate clathrate and then of a saturated clathrate between a substrate (guest) and a receptor (host), which breaks the sensor response into two separate steps. The corresponding host–guest pseudopolymorphism allows the discrimination of a target substrate in complex mixtures using a single gravimetric sensor. This mechanism does not require for a substrate to have multiple functional groups for a complementary host–guest binding. Moreover, qualitative and quantitative molecular recognition of hydrocarbon in the mixtures with its close homologues can be achieved. Such ability was performed in the present work for a thiacalix[4]arene derivative coating of a quartz-microbalance sensor, which is able to recognize benzene in the headspace of its liquid mixtures with toluene, xylenes, ethylbenzene, water, nitriles, alcohols and other compounds. The pseudopolymorphism of host–guest clathrate and low-temperature polymorphism of the host was confirmed by the determination of vapor sorption isotherms, thermoanalysis and X-ray powder diffraction analysis of the host–guest saturation products.

1. Introduction

The usual vapor sensing mechanism of mass-sensitive sensors includes only a simple vapor–liquid or vapor–solid partition, whose selectivity is insufficient for effective discrimination of a mixture component with similar structure [1,2]. Unlike chromatographic separation, where molecular structure and concentration of the analyte have influence on the different parameters of the chromatogram [3], a typical response of a QCM sensor gives only one parameter, which is proportional to the product of the substrate concentration and partition coefficient [4,5]. Such behavior is valid for various kinds of receptors including isotropic polymers [1,4], molecularly imprinted polymers (MIPs) [6,7] and clathrate-forming hosts previously studied [8–16]. The lack of substrate-related information in this experiment requires sensor arrays even for analysis of pure vapors [17].

Additional possibilities for vapor recognition can be found in the cooperativity of guest inclusion by clathrate-forming hosts [8,18,19]. In a thermally stable state, these hosts have vapor sorption isotherms of sigmoidal shape reflecting the phase transition of clathrate formation [8,12,13,18–21]. Such a shape gives better molecular recognition, having at least two substrate-related parameters: the inclusion threshold by the substrate (guest) relative vapor pressure and the guest inclusion stoichiometry [18,19]. Earlier studies did not report any related cooperative behavior of clathrate-forming hosts in sensor responses, which had the same shape as with isotropic polymers and MIPs [5–7]. The problem is in the prolonged high temperature treatment of a receptor, which is not suitable in sensor experiments but is the necessary precondition for reproducible determination of sorption isotherms in systems with solid host and guest vapor [8,18–20]. The solid host regenerated by low-temperature elimination of the guest, being generally a mixture of a number of undefined non-equilibrium forms with different packing, does not exhibit cooperativity of guest inclusion [20,22–24].

In some cases, this problem may be overcome. For example, the hydration of amorphous cross-linked polyacrylamide derivative enables it with the binding cooperativity for hydrophobic substrates [25]. The other option is the use of clathrate pseudopolymorphism with two steps of clathrate formation. In the first step, the formation of the intermediate clathrate makes the receptor more homogeneous so that the second step in the sensor response can be observed, corresponding to the saturated clathrate formed.

In the present work, we report the first application of clathrate pseudopolymorphism in vapor sensors. This phenomenon affects the guest-binding kinetics by the host, depending

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