

Thermodynamics of benzotriazole derivatives sorption from water-organic eluents

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Abstract

The temperature dependence of the benzotriazole derivatives chromatographic retention on hypercrosslinked polystyrene from water-acetonitrile eluent with different acetonitrile content was studied. It has been shown that the retention of benzotriazole derivatives on the surface of hypercrosslinked polystyrene is generally subject to the laws of the reversed-phase variant of HPLC. At the same time, the dispersion interactions of the heteroaromatic fragment with the sorbent surface make the main contribution to the chromatographic retention; however, the presence of functional groups of different chemical nature in the main heteroaromatic fragment leads to significant variations in the sorption characteristics, which are also determined by the composition of the eluent. From the experimentally determined thermodynamic characteristics of the sorption of benzotriazole derivatives, it follows that the change values of the standard molar enthalpy and Gibbs energy of sorption during the transition of the molecules of the studied analytes from the bulk solution to the surface layer of the HCPS are negative. This fact testifies to the exothermicity of the process and its spontaneous flow. The values of thermodynamic parameters of the studied derivatives vary in a relatively narrow range and are determined mainly by the nature of the substituent and its position in the heterocycle, remaining generally not as significant as the magnitude of the retention factor. Based on the analysis of the calculated enthalpy and Gibbs energy of sorption values, the influence of the functional groups nature on the studied substances retention was established, as well as differences in the values of thermodynamic values for compounds with electron-donating and electron-accepting substituents capable of π -interactions with the surface of supershyne polystyrene and the formation of a hydrogen bond with the components mobile phase. The absence of the effect of entropy-enthalpy compensation associated with competitive interactions of sorbates with the surface of the sorbent and the bulk phase of the eluent is demonstrated. The dependence of the thermodynamic characteristics of sorption on the structural and topological parameters of sorbate molecules was studied. The influence of the stereochemistry of sorbate molecules, changing under the influence of polar molecules of the components of the mobile phase, on confinement has been established. It is shown that the change in the Gibbs energy of sorption and the values of the surface area and the projection of the surface area of molecules onto the sorbent plane is simulated due to the increased interaction of sorbate molecules having a large surface due to π -stacking.

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