

Thermodynamics of benzotriazole derivatives sorption from water-organic eluents

© Sara A. Dzhabieva,¹ Dilgam B. Tagiev,¹ Nizami A. Zeinalov,¹ and Svetlana V. Kurbatova^{2*†}

¹M. Naghiyev Institute of Catalysis and Inorganic Chemistry. Azerbaijan National Academy of Sciences, 113 H. Javid Ave. AZ1143, Baku. Azerbaijan.

²Samara National Research University. Acad. Pavlova St., 1. Samara, 443011. Russia.
Факс: +7 (846) 334-54-17. E-mail: curbatsv@gmail.com

*Supervising author; †Corresponding author

Keywords: benzotriazole derivatives, high performance liquid chromatography, hypercrosslinked polystyrene, sorption thermodynamics, water-acetonitrile eluent, sorption enthalpy, Gibbs energy of sorption.

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.

References

- [1] V.D. Shatts, O.V. Sakhartova. High Performance Liquid Chromatography: Fundamentals of Theory. Methodology. Use in medicinal chemistry. Riga: Zinatne. **1988**. 390p.
- [2] S. Bocian, P. Vajda, A. Felinger, B. Buszewski. Solvent excess adsorption on the stationary phases reversed-phase liquid chromatography with polar functional groups. *J. Chromatogr. A* **2008**. Vol.1204. P.35-41.
- [3] F. Gritti, G. Guiochon. Thermodynamics of adsorption of binary aqueous organic liquid mixtures on a RPLC adsorbents. *J. Chromatogr. A* **2007**. Vol.1155. P.85-99.

- [4] G. Vanhoenacker, A. Dos Santos Pereira, T. Kotsuka, D. Cabooter, G. Desmet, P. Sandra. Evaluation of a new polymeric stationary phase with reversed-phase properties for high temperature liquid chromatography. *J. Chromatogr. A*. **2010**. Vol.1217. No.19. P.3217-3222.
- [5] J. Acosta, A. Arce, E. Rodil, A. Soto. A thermodynamic study on binary and ternary mixtures of acetonitrile, water and butyl acetate. *Fluid Phase Equilib.* **2002**. Vol.203. No.1-2. P.83-98.
- [6] A. Wang, P.W. Carr. Comparative study of the linear solvation energy relationship, linear solvent strength theory, and typical-conditions model for retention prediction in reversed-phase liquid chromatography. *J. Chromatogr. A* **2002**. Vol.965. P.3-23.
- [7] N.M. Dummer. 4(5)-Methylbenzotriazole: a review of the life-cycle of an emerging contaminant. *Rev. Environ Sci. Biotechnol.* **2014**. Vol.13. P.53-61.
- [8] S.A. Dzhabieva, S.V. Kurbatova. The influence of the nature of the sorbent on the retention of benzotriazole derivatives under RP HPLC conditions. *Journal of Physical Chemistry (Rus)*. **2015**. Vol.89. No.10. P.1644-1650. (russian)
- [9] S.A. Dzhabieva, S.V. Kurbatova, E.A. Kolosova. The influence of the topology of the molecules of benzotriazole derivatives on their chromatographic retention under RP HPLC conditions. *Journal of structural chemistry*. **2017**. Vol.58. No.3. P.484-493. (russian)
- [10] V.P. Belousov, M.Yu. Panov. Thermodynamics of aqueous solutions of non-electrolytes. *Leningrad: Chemistry*. **1983**. 264p. (russian)
- [11] Y. Rao, N.J. Turro, K.B. Eisenthal. Water Structure at Air/Acetonitrile Aqueous Solution Interfaces. *J. Phys. Chem.* **2009**. Vol.113. P.14384-14389.
- [12] G.R. Behbehani, S. Ghamamy, W.E. Waghorne. Enthalpies of transfer of acetonitrile from water to aqueous methanol, ethanol and dimethylsulphoxide mixtures at 298.15 K. *Thermochimica Acta*. **2006**. Vol.448. No.1. P.37-40.
- [13] B.R. Sayfutdinov, V.A. Davankov, M.M. Il'in. Thermodynamic characteristics of the adsorption of 1,3,4-oxadiazoles and 1,2,4,5-tetrazines from methanol and water-methanol solutions on hyper-crosslinked polystyrene. *Journal of Physical Chemistry*. **2017**. Vol.91. No.3. P.539-543. (russian)
- [14] R. Ranatunga, M.F. Vitha, P.W. Carr. Mechanistic implications of the equality of compensation temperatures in chromatography. *J. Chromatogr. A* **2002**. Vol.946. No.1-2. P.47-49.
- [15] V.A. Davankov, C.S. Sychov, M.M. Ilyin, K.O. Sochilina. Hypercrosslinked polystyrene as a novel type high-performance liquid chromatography column packing material. Mechanisms of retention. *J. Chromatogr. A* **2003**. Vol.987. P.67-75.
- [16] J. Horak, N.M. Maier, W. Lindner. Investigations on the chromatographic behavior of hybrid reversed-phase materials containing electron donor-acceptor systems. II. Contribution of π - π aromatic interactions. *J. Chromatogr. A* **2004**. Vol.1045. P.43-58.
- [17] M.H. Abraham, A. Ibrahim, A.M. Zissimos. Determination of sets of solute descriptors from chromatographic measurements. *J. Chromatogr. A* **2004**. Vol.1037. P.29-47.
- [18] G.N. Chuev, M.V. Bazilevsky. Molecular models of solvation in polar liquids. *Russian Chemical Reviews*. **2003**. Vol.72. No.9. P.827-851. (russian)