

## Retention of tetrahydroquinoline derivatives on hypercross-linked polystyrene under conditions of liquid chromatography from weakly polar eluents

© Nadezhda A. Nekrasova,<sup>1</sup> Svetlana V. Kurbatova,<sup>1\*</sup> and Margarita N. Zemtsova<sup>2</sup>

<sup>1</sup> Department of Physical Chemistry and Chromatography. Samara National Research University. Academic Pavlov St., 1. Samara, 443011. Russia. Phone: +7 (846) 334-54-32. E-mail: curbatsv@gmail.com

<sup>2</sup> Department of Organic Chemistry. Samara State Technical University. Kuybyshev St., 153. Samara, 443010. Russia. Phone: +7 (846) 332-21-22.

\*Supervising author; <sup>+</sup>Corresponding author

**Keywords:** water-organic solutions, water – acetonitrile mixture, tetrahydroquinoline derivatives, potentiometry, determination of ionization constants, conductivity, refractometry.

### Abstract

The paper presents the results of study of the retention regularities of 1,2,3,4-tetrahydroquinoline derivatives under conditions of quasi-normal-phase high performance liquid chromatography. A feature of this chromatographic mode is the predominant contribution of specific interactions with the sorbent – hypercrosslinked polystyrene in our case – to the retention. The choice of sorbent due to its widespread use as an adsorbent in liquid chromatography, as well as its ability to participate in  $\pi$ -interactions.

It was found, that the nature of the non-polar eluent modifier has a significant effect on retention: it increases in the range dichloromethane – tetrahydrofuran – isopropanol. The difference in the elution strength of the solvents is explained by the difference in their ability to specific interactions with both sorbate molecules and the surface of hypercrosslinked polystyrene.

When the content of the modifier changes, the sorption characteristics decrease with increasing polarity of the resulted eluent due to increasing of the specific sorbate – eluent interactions contribution, and decreasing of the role of sorbate – sorbent  $n$ - $\pi$  interactions. The decrease in the contribution of specific interactions to sorption leads, particularly, to the fact that the retention factor values of different compounds noticeably come closer.

The dependences of retention on physicochemical parameters of the sorbates turn out to be inverse with respect to the regularities characteristic of the reversed-phase mode. Reversed-phase retention usually increases with increasing volume, polarizability and lipophilicity of sorbate molecules due to enhanced dispersion interactions with the sorbent and solvophobic – with the polar eluent, while in the quasi-normal-phase conditions retention decreasing is observed with increasing of these characteristics. The most probable reason for this is the enhancement of dispersion interactions with the non-polar mobile phase and the absence of solvophobic effects in the latter case.

Comparison of the retention factors of sorbates containing different functional groups showed that compounds containing phenyl fragments have not characterized by the highest retention factor values, as might be expected based on their ability to  $\pi$ - $\pi$ -interactions with the surface of hypercrosslinked polystyrene. This can be explained by the non-planar orientation of the phenyl substituents, which, in the absence of the “pressing” action of the mobile phase, does not allow for the realization of all possible  $\pi$ - $\pi$  interactions with the sorbent. Specific interactions of hypercrosslinked polystyrene with tetrahydroquinoline derivative molecules are carried out mainly due to  $\pi$ - and  $n$ - $\pi$ -interactions with oxo-groups of sorbates, which is manifested in a greater retention of compounds containing an oxo-group in position 2 compared to similar derivatives with methyl radical in this position.

### References

- [1] N.A. Penner, P.N. Nesterenko, M.M. Hyin, et al. Investigation of the properties of hypercrosslinked polystyrene as a stationary phase for high-performance liquid chromatography. *Chromatographia*. **1999**. Vol.50. No.9-10. P.611-620.
- [2] N.E. Oro, C.A. Lucy. Comparison of hypercrosslinked polystyrene columns for the separation of nitrogen group-types in petroleum using High Performance Liquid Chromatography. *J. Chromatogr. A* **2010**. Vol.1217. No.40. P.6178-6185.

- [3] J. Huang, S.R. Turner. Hypercrosslinked Polymers: A Review. *Polym. Rev.* **2018**. Vol.58. No.1. P.1-41.
- [4] C.S. Sychov, M.M. Ilyin, V.A. Davankov, et al. Elucidation of retention mechanisms on hypercrosslinked polystyrene used as column packing material for high-performance liquid chromatography. *J. Chromatogr. A* **2004**. Vol.1030. No.1-2. P.17-24.
- [5] V.A. Davankov, C.S. Sychov, M.M. Ilyin, et al. Hypercrosslinked polystyrene as a novel type of high-performance liquid chromatography column packing material. Mechanisms of retention. *J. Chromatogr. A* **2003**. Vol.987. P.67-75.
- [6] S.V. Prokopov, E.V. Tyrina, V.A. Davankov and others. Quasinormal phase chromatography of nitrogen-containing adamantane derivatives. *Journal of Physical Chemistry.* **2013**. Vol.87. No.1. P.99-105. (russian)
- [7] V.D. Shatts, O.V. Sakhartova. High Performance Liquid Chromatography: Fundamentals of Theory. Methodology. Use in medicinal chemistry. *Riga: Zinatne.* **1988**. 390p.
- [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.* **2015**. Vol.89. No.10. P.1644-1650. (russian)
- [9] X. Zhang, H. Li, L. Zhang, et al. Porous organic cage embedded C18 amide silica stationary phase for high performance liquid chromatography. *Anal. Sci.* **2018**. Vol.34. No.4. P.445-451.
- [10] X. Wang, H. Peng, J. Peng, et al. Preparation and evaluation of a polar embedded diphenylethene bonded stationary phase for High Performance Liquid Chromatography. *Microchem. J.* **2018**. Vol.142. P.195-201.
- [11] B.R. Sayfutdinov, V.A. Davankov, M.M. Il'in. et al. Selective adsorption of organic compounds from solutions on ultracrosslinked polystyrenes with limiting degrees of crosslinking. *Physicochemistry of the surface and protection of materials.* **2015**. Vol.51. No.6. P.601-608. (russian)
- [12] N.A. Nekrasova, S.V. Kurbatova, M.N. Zemtsova. Regularities of sorption of 1,2,3,4-tetrahydroquinoline derivatives from water-acetonitrile solutions on non-polar sorbents. *Sorption and chromatographic processes.* **2016**. Vol.16. No.2. P.154-162. (russian)