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# RELATIONSHIP BETWEEN THERMODYNAMIC PARAMETERS AND RETENTION MECHANISM FOR POLAR COMPOUNDS IN HYDROPHILIC INTERACTION LIQUID CHROMATOGRAPHY

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Retention of analytes in hydrophilic interaction liquid chromatography (HILIC) is governed by partitioning, adsorption, and ion exchange mechanisms. The contribution of each one depends on the structure of the stationary phase, the nature of the analyte, and the mobile phase composition. Understanding the processes in chromatographic system is important for successful selecting of separating conditions for complex mixtures. Therefore, evaluation of the retention mechanism is an urgent task in HILIC. In other methods such as reversed phase HPLC or gas chromatography, the determination of the retention mechanism is based on the calculation of thermodynamic parameters using van't Hoff equation. The dependence of the natural logarithm of the retention factor on the inverse temperature is described by the equation [1]:

$$lnk' = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} + \ln\left(\frac{V_s}{V_m}\right),$$

where $\Delta H^o$, $\Delta S^o$ is the change of standard molar enthalpy and entropy of substance transfer from the mobile to the stationary phase; $V_s$ is the volume of the stationary phase; $V_m$ is the volume of the mobile phase. At the moment there is the lack of works aimed at comparing the obtained thermodynamic values with the prevailing retention mechanism in HILIC.

In this work, we determined the thermodynamic retention values for various test compounds (nitrogenous bases, quaternary ammonium salts, sulfonic acids, weak acids and bases) on 3-aminopropyl silica in HILIC mode, varying the column temperature in the range from 25 to 55 °C. The experiments were performed at two eluting ion concentrations of 2.5 and 5 mM for each mobile phase composition: acetonitrile / formate (pH 2.85) or acetate (pH 5.76) buffer solution, 90/10 vol%. The aim of this work was to reveal the effects of mobile phase pH and concentration, and the analyte structure on thermodynamic parameters.

When using formate buffer solution with pH 2.85, amino groups of the stationary phase were fully protonated, so the main contribution to the retention of negatively charged analytes (sulfonic acids) was made by ion exchange. It led to the increase of their retention times with enhancing column temperature. As the concentration of the eluting ion increased, an increase of the enthalpy of transfer was observed due to the decrease of the contribution of electrostatic interactions. Also, the enthalpy was affected by the hydrophobicity of the analyte. Zero enthalpy values were obtained for weak bases, indicating an entropy-controlled process. Negative enthalpy values were estimated for the other substances, indicating exothermicity of the transfer process from the mobile to the stationary phase and a contribution of partitioning and adsorption to retention. Using acetate buffer solution (pH 5.76) led to deprotonation of a part of amino groups of the stationary phase. It resulted in increased retention enthalpy values for most of the analytes. Nonlinearity of temperature dependences was observed for sulfonic acids due to changing retention mechanism with temperature increase.

The different influence of column temperature on the retention times of the analytes resulted in the changes of separation selectivity for the mixture of test substances. Increasing the column efficiency with increasing temperature was also observed. Some critical pairs of compounds were better separated under higher column temperature.

## References

[1] *Analytica Chimica Acta.* **2015**, 70

[2] *Food Chem.* **2018**, *248*, 70

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