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Effect of temperature on competitive adsorption of the solute and the organic solvent in reversed-phase liquid chromatography

Izabela Poplewska, Wojciech Piątkowski, Dorota Antos *

Department of Chemical and Process Engineering, Rzeszów University of Technology, 6 Powstańców Warszawy Avenue, 35-959 Rzeszów, Poland

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Abstract

In analysis of the temperature effect on chromatographic separations the influence of the adsorption of organic solvent on the retention properties of solute is generally not taken into account. In fact, adsorption behavior of solutes is strongly affected by competitive adsorption of organic solvents, which is temperature dependent. In this work changes of adsorption equilibrium of an organic solvent as well as a solute with temperature have been analyzed. Data of the excess adsorption of methanol from aqueous solutions on octadecyl-bonded silica have been acquired at different temperature. Experiments have been performed over a relatively narrow temperature range corresponding to typical chromatographic conditions, i.e., 10–50 °C. The competitive adsorption equilibria of model solutes (i.e., two homologous compounds: cyclopentanone and cyclohexanone) have been measured at different temperature and composition of the mobile phase. Temperature alterations to the retention properties were found to result from combined effects of changes in adsorption behavior of the organic solvent and of the solute. The influence of temperature on the separation selectivity has been considered.

Keywords: Temperature effects; Solvents strength; Retention model; Excess adsorption; Modeling of band profiles

1. Introduction

Mobile phase composition and column temperature are operating variables commonly used to control adsorption behavior in reversed phase chromatography. Several studies have been performed to compare the effect of a modulation of mobile phase composition to that of the temperature (e.g. [1–3]). It is established that the temperature is a less effective operating parameter for reduction of retention compared to the solvent strength. Strong temperature effects are evidenced only for ionizable compounds, therefore, manipulating of the temperature is a useful tool mainly in ion exchange and ion-pair chromatography [2]. For neutral components a change of 4–5 °C in temperature corresponds to approximately 1% changes in composition of mobile phase [1,2]. Moreover, the temperature range of interest is usually from ambient temperature up to 50–60 °C since classical bonded silica stationary phases are thermally unstable and operating at higher temperature requires employing unique new generation columns offering possibility to carry out high temperature experiments. The use of higher temperature can also cause decomposition of temperature labile solutes.

However, combining solvent strength and temperature can have a powerful effect on the separation effectiveness in RP chromatography in terms of improving selectivity of the separation and the column efficiency. The acceptance of importance of temperature is based on well-known effects of decrease in viscosity of the mobile phase and increase in solute diffusivity. The first effect leads to lowering backpressure over the column allowing increasing the flowrate. This benefits in improvement of the process productivity, which is directly related to speed of the separation process. The consequence of increased diffusivity is faster mass transport kinetics, which is reported to result in improvement of column efficiency. Moreover, as reported in [4–7] separation efficiency can be increased by cooling eluent to a temperature few degrees below that of the column, which leads to a change in the direction of radial temperature gradient and to inversion of flow profile. On the other hand it has been evidenced that poor eluent preheating or ineffective thermal equilibration of the mobile phase in column causes band broadening and peak

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* Corresponding author. Tel.: +48 17 865 1730.
E-mail address: Dorota_Antos@prz.edu.pl (D. Antos).

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distortion due to radial temperature gradients inside the column [8,9].

The state of the art concerning the active use of elevated temperatures in liquid chromatography was summarized in [10]. The review of the chemical and thermal stability of RP stationary phase was presented in [11].

In order to optimize the separation, it is necessary to predict adsorption behavior under diverse conditions corresponding to different combinations of operating variables, e.g., different temperature and mobile phase properties. For optimization of operating conditions an adequate model to describe adsorption as a function of these variables is indispensable. To predict the effect of the mobile phase composition the linear solvent strength theory (LSST) developed by Snyder and co-workers [12,13] is widely used. According to the LSST model, the retention factor k'_0 of a solute is related to the solvent composition, ϕ, by the following equation:

$$\ln k'_0 = \ln k_\mathrm{w} - \Psi\phi \tag{1}$$

where Ψ is the solvent strength parameter, ϕ the volume fraction of the stronger solvent and k_w is the retention factor of the solute in a pure weak solvent.

The retention factor k'_0 is correlated with the slope of the isotherm of the solute at infinite dilution ($c \to 0$):

$$k'_0 = F \left.\frac{\partial q^*}{\partial c}\right|_{c\to 0} = FH \tag{2}$$

where $F = (1 - \varepsilon_\mathrm{t})/\varepsilon_\mathrm{t}$ is the phase ratio and H is the Henry constant.

For prediction of the temperature effect on retention behavior the van't Hoff equation can be used:

$$\ln k = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} + \ln F \tag{3}$$

where ΔH^0 and ΔS^0 are the enthalpy and entropy change associated with the transfer of solute from one phase to another, R the gas constant, T the temperature and F is the phase ratio.

Thermodynamics of retention process were investigated in [14] where the use of superheated water as the mobile phase was explored. The influence of the temperature on the thermodynamic coefficients was analyzed in [3,15].

In order to simulate nonlinear chromatography at different temperature and the mobile phase composition the mentioned above retention models are not sufficient. In order to estimate the process efficiency band profiles registered under conditions of a strong mass overloading should be correctly reproduced.

For optimization of the mobile phase composition in nonlinear chromatography realized at isocratic as well as at gradient mode an empirical or semi-empirical approach is typically employed. This approach consists in determining of the adsorption equilibrium of the solute at different mobile phase composition and correlating the values of all the isotherm coefficients with the concentration of the organic solvent by dependencies related to Eq. (1) [16–19]. This approach was extended to account for possible adsorption of the modifier in [20,21].

Similar approach is used for quantifying temperature effect on the adsorption behavior under conditions of a nonlinear isotherm. The effect of temperature on the isotherm parameters have been studied by Kim et al. [22] who analyzed changes of adsorption equilibrium with temperature by determining the isotherm parameters of a solute at different temperatures.

All the models mentioned concerning both the process variables, i.e., elution strength as well as temperature do not take into account the influence of competitive adsorption of a strong solvent on the adsorption behavior of solute. In our studies [23–25], the adsorption of a strong solvent has been analyzed and a model of competitive adsorption of solute–solvent has been proposed. In these studies the adsorption of a strong solvent has been determined on the basis of experimental data of excess adsorption. The model of competitive adsorption proposed allowed prediction of changes of band shapes with variation of the mobile phase composition. Such an approach was adopted for studying both the reversed-phase [23,24] and normal-phase [25] systems. Because of structural complexity of bonded silica phases the competition model for a reversed-phase system was found to be more complicated compared to that suggested for adsorption on the ordinary silica in a normal-phase system.

In this work this analysis was extended by considering the effect of temperature on the adsorption equilibria of the organic solvent and on the resulting competitive adsorption of the solute. The combined effect of solvent strength and temperature on the separation selectivity was studied. The study was performed in a reversed-phase system.

2. Theory

2.1. *Adsorption equilibria of the organic solvent*

The adsorption model assumes that molecules of organic solvent can interact creating multilayer in the adsorbed surface [23]. Dual Langmuir type of adsorption mechanism is assumed to take place on each layer: displacement on a polar surface of uncovered silica and partition on non-polar alkyl chains. The term "adsorption" is here understood as a general process of transferring solutes between two phases; "displacement" and "partition" are specific mechanisms of adsorption.

A detailed discussion concerning the model can be found in [23]; in the following only the final expressions of the isotherm equations are presented.

According to the displacement mechanism the adsorbed amount of organic solvent A in binary mixtures with water B is expressed as:

$$(q_\mathrm{A}^*)_\mathrm{d} = (q_\mathrm{A}^\infty)_\mathrm{d}(x_\mathrm{A}^\mathrm{s})_\mathrm{d} = \frac{(q_\mathrm{A}^\infty)_\mathrm{d} K_\mathrm{d1}\, x_\mathrm{A}^\mathrm{m}\gamma_\mathrm{A}^\mathrm{m}}{(1 - x_\mathrm{A}^\mathrm{m})\gamma_\mathrm{B}^\mathrm{m} + K_\mathrm{d1}\, x_\mathrm{A}^\mathrm{m}\gamma_\mathrm{A}^\mathrm{m}} \times \frac{1 - ((K_{\mathrm{d}n}\, x_\mathrm{A}^\mathrm{m}\, \gamma_\mathrm{A}^\mathrm{m})/((1 - x_\mathrm{A}^\mathrm{m})\gamma_\mathrm{B}^\mathrm{m} + K_{\mathrm{d}n} x_\mathrm{A}^\mathrm{m}\gamma_\mathrm{A}^\mathrm{m}))^{n_\mathrm{d}}}{1 - ((K_{\mathrm{d}n}\, x_\mathrm{A}^\mathrm{m}\, \gamma_\mathrm{A}^\mathrm{m})/((1 - x_\mathrm{A}^\mathrm{m})\gamma_\mathrm{B}^\mathrm{m} + K_{\mathrm{d}n}\, x_\mathrm{A}^\mathrm{m}\gamma_\mathrm{A}^\mathrm{m}))} \tag{4}$$

where $x_{\mathrm{A}i}^\mathrm{s}$ is the fraction of surface coverage in *i*th layer: $x_{\mathrm{A}i}^\mathrm{s} = q_{\mathrm{A}i}/q_\mathrm{A}^\infty$ for $i = 1, \ldots, n$, q_A^∞ the maximal loading in each layer, hence, the maximal amount adsorbed in n layers is equal to nq_A^∞,