Journal of Chromatography A, 1460 (2016) 147–152

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Kinetic performance of stationary phases for gas chromatography based on poly(oligoethyleneglycoldiacrylate)

A. Korolev, V. Shyrayeva, T. Popova, A. Kanateva, A. Kurganov*

Topchiev Institute of Petrochemical Synthesis RAS, 119991 Lenin Av. 29, Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 12 May 2016
Received in revised form 4 July 2016
Accepted 5 July 2016
Available online 6 July 2016

Keywords:
Gas chromatography
Stationary phase
Kinetic performance
Polymer

ABSTRACT

Open capillary columns with polymeric stationary phases based on poly(oligoethyleneglycoldiacrylate) were prepared and tested on their kinetic performance. Stationary phases prepared with low molar mass monomers were inferior to stationary phases based on high molar mass monomers. Structure of these stationary phases appeared to be favorable for solute diffusion in the stationary phase. These columns were also characterized by improved kinetic performance limit. Stationary phase based on poly(ethylenglycol) and prepared according to the traditional procedure, demonstrated average kinetic performance. Optimal kinetic performance limit curves characterizing the prepared stationary phases were evaluated in this work using new simple procedure based on extraction of optimal values from the corresponding matrix. This technique makes it possible to evaluate optimal kinetic performance limit curves without any additional simplifications and cumbersome calculations.

1. Introduction

Poly(ethylenglycol) (PEG) is one of the most widely used polar stationary phase in gas chromatography (GC). Polymer deposited onto capillary column walls is commonly subjected to crosslinking to increase the thermal stability of the stationary phase. The crosslinking is performed by adding of a radical polymerization initiator (e.g. dicumyl peroxide) during the formation of PEG layer on the column walls with subsequent heating of the column. From polymeric point of view PEG is not a polymer suitable for crosslinking because it does not contain any unsaturated groups. Nevertheless, the result of the procedure is the formation of non-soluble polymeric layer in the column, and such "crosslinking" of PEG is widely used in column manufacturing [1]. However, the structure of the crosslinked polymer and an impact of such a crosslinking on the column separation properties remain under discussion.

An alternative way to get the crosslinked PEG stationary phases is usage of polymers containing unsaturated groups capable of crosslinking under the influence of free radicals. Suitable monomers for preparation of corresponding polymers are oligoethylenglycoldiacrylates. These monomers were already used for preparation of stationary phases in liquid chromatography [2–4]. However, in GC they have not been investigated yet. This paper describes preparation of new stationary phases for GC based on oligoethylenglycoldiacrylates and comparison of their kinetic properties with those of the standard PEG columns.

A comparison of different columns will be commonly made under "identical conditions". However, such a comparison is not fair because each column can better disclose its potential being used under optimal conditions. An opportunity to compare columns under their optimal conditions is provided by the so-called kinetic plot method [5]. The theory of kinetic plots was initially developed in the 60-s [6], but only nowadays, due to intensive research performed by Desmet and his group [7–10], kinetic plots were recognized as an effective tool for quality evaluation of different packings and columns [11,12]. In general, a kinetic plot provides a relationship between the column efficiency N and the analysis time t_R. Under the optimal conditions kinetic plots describe the best column performance in a single curve, i.e. the highest value of the column efficiency that can be obtained within the shortest analysis time at the optimal pressure drop. This is the so-called kinetic performance limit [5]. It is necessary and sufficient for the LC system to work at the maximal pressure drop allowable for the system [6,7,13,14] to reach the kinetic performance limit (KPL). The optimal column pressures corresponding to KPL in GC have to be found using the standard mathematical procedure: evaluating partial derivative of KPL equation with respect to column pressure, setting the derivative to zero and solving the obtained

* Corresponding author at: Topchiev Institute of Petrochemical Synthesis RAS, Russia, 119991 Moscow, Lenin Av. 2, Russian Federation.
E-mail address: kurganov@ips.ac.ru (A. Kurganov).

http://dx.doi.org/10.1016/j.chroma.2016.07.010
0021-9673/

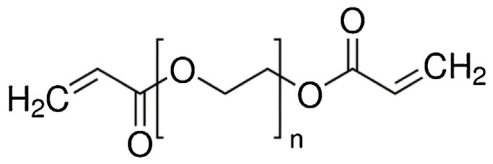

Fig. 1. Structure of monomers used for preparation of stationary phases.

equation. Unfortunately, this straightforward procedure resulted in very bulky expressions which have not been evaluated so far. Giddings [6] considered a special case of KPL equation assuming outlet column pressure p_o equal to zero. Jespers et al. [7] simplified KPL equation by neglecting coefficient C_S in Van Deemter equation and setting Giddings compressibility factor used in Van Deemter equation equal to unity. Such a simplification is acceptable while discussing the kinetic properties of columns; however it underestimates the impact of solute/stationary phase interaction on column performance. Despite the accepted simplifications, the authors [7] did not demonstrate the analytical expression for optimal KPL. Instead of this, they suggested a two-step procedure for evaluation of the optimal KPL curve. In a first step a set of optimal column pressures is calculated for the given plate count and then in a second step corresponding t_m values are calculated point-by-point for each pair of N-$p_{i,opt}$ values.

The main aim of the paper is to evaluate the kinetic performance of new different stationary phases prepared by polymerization of oligoethylenglycoldiacrylates. A simple procedure for evaluating optimal KPL plots without taking any simplifications is developed and presented in the paper.

2. Experimental

2.1. Measurements

Shimadzu GC-17A gas chromatograph with FID detector and split/splitless injector was used. The He carrier gas was used through all the measurements. The maximum pressure drop of this system was 400 kPa and the outlet pressure was always equal to atmospheric. The test mixture contained methane and o-xylol. Injection of 1 μL sample was done at 250 °C and 50:1 split ratio. Separations were performed under isothermal conditions with the flow varying between 0.2 and 1.2 mL/min and oven temperature set at 80 °C. The detector temperature was set at 300 °C, H_2 flow at 40 mL/min, air flow at 300 mL/min and make-up flow at 20 mL/min. Data were analyzed with EcoChrom program (BoySoft, Russia).

2.2. Column preparation

All columns were prepared by dynamical coating of quartz capillary with I.D. 0.16 mm and length of 10 m with polymerization mixture. All monomers – oligoethyleneglycoldiacrylates (Fig. 1) – were of chemically pure grade and were received from Sigma–Aldrich (St. Louis, MO, United States). Properties of monomers are shown in Table 1. Polymerization mixture was prepared by dissolution of monomer (concentration 3–5% w/w) and initiator azobis(isobutyronitrile) or dicumylperoxide (1–5% w/w from monomer mass) in chloroform. The capillary was filled with the polymerization mixture and sealed at one end. The open end of the capillary was inserted into drawing machine and dragged through the heating block. The heating unit had temperature of 130 °C at the entry point and 90 °C inside the thermostat. The whole capillary was dragged though the heating block and then was left in the thermostat at 90 °C for 1 h to complete polymerization. Afterwards the capillary was taken out from thermostat, the sealed part was cut off, and the capillary was washed out with methylene chloride and was dried in a stream of helium. The average thicknesses of deposited polymeric films were evaluated by weighting the column before and after the polymer layer deposition and are shown in Table 1.

3. Result and discussion

3.1. Evaluation of optimal kinetic plot

Kinetic plot equation is commonly derived from combination of Van Deemter and Poiseuille-Darcy equations [6,7,15,16] and the final form of kinetic plot equation in GC is [14]:

$$t_m = \left[\frac{-S_1 + \sqrt{S_1^2 - 4S_3\left(S_2 - N^{-1}\right)}}{2\left(S_2 - N^{-1}\right)}\right]^2 \quad (1)$$

where

$$S_1 = \frac{9}{4\sqrt{3}} A \frac{p_i^4 - p_o^4}{\left(p_i^3 - p_o^3\right)^{1.5}} \sqrt{\frac{\eta}{K_V}} \quad (2)$$

$$S_2 = \frac{9}{4} B \frac{p_i^4 - p_o^4}{\left(p_i^3 - p_o^3\right)^2} \frac{\eta}{K_V} \quad (3)$$

$$S_3 = \frac{3}{4} C_m \frac{p_i^4 - p_o^4}{p_i^3 - p_o^3} + C_s \quad (4)$$

Here t_m is elution time of a non-retained compound, η is mobile phase viscosity, K_V is column permeability, A, B, C_m and C_s are the coefficients of Van Deemter equation; p_i and p_o are the inlet and outlet column pressures. Coefficient A is zero for open capillary columns [18] and Eq. (1) is simplified to:

$$t_m = \frac{S_3}{N^{-1} - S_2} = \frac{\frac{3}{4} C_m \frac{p_i^4 - p_o^4}{p_i^3 - p_o^3} + C_s}{N^{-1} - \frac{9}{4} B \frac{\left(p_i^4 - p_o^4\right)\eta}{K_V\left(p_i^3 - p_o^3\right)^2}} \quad (5)$$

To use Eq. (5) one has to evaluate the coefficients of Van Deemter equation first of all. Because of compressibility of moving phase in GC an extended form of Van Deemter equation suggested by Giddings [6] has to be used:

$$H = \frac{B f_G}{u_o p_o} + C_m f_G u_o p_o + C_S u_o f_M \quad (6)$$

Here f_G and f_M are the compressibility factors given by Giddings and by Martin correspondingly:

$$f_G = \frac{9\left(P^4 - 1\right)\left(P^2 - 1\right)}{8(P^3 - 1)^2} \quad (7)$$

$$f_M = \frac{3\left(P^2 - 1\right)}{2\left(P^3 - 1\right)} \quad (8)$$

where $P = p_i/p_o$ is relative pressure.

Eq. (6) presents the height equivalent to the theoretical plate (HETP, H) as a function of three variables u_o, p_i and p_o which makes unpractical evaluation of Van Deemter coefficients using this relationship. The number of independent variables in Eq. (6) can be reduced to two by means of replacement of variables [17]:

$$H = B_1 \frac{\left(p_i^4 - p_o^4\right)}{\left(p_i^3 - p_o^3\right)^2} + C_{1m} \frac{\left(p_i^4 - p_o^4\right)\left(p_i^2 - p_o^2\right)^2}{\left(p_i^3 - p_o^3\right)^2} + C_{1S} \frac{\left(p_i^2 - p_o^2\right)^2}{\left(p_i^3 - p_o^3\right)} \quad (9)$$

Outlet column pressure remained constant through all the measurements (atmospheric pressure) in this research and, therefore,