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Measurement of pore diffusivity of *R*,*S*-α-Tetralol enantiomers in chiral adsorbent CHIRALPAK AD by zero length column method

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Abstract

The zero length column (ZLC) technique for measurement of pore diffusivity in chiral adsorbent CHIRALPAK AD with particle size 20 and 50 μm at temperature of 25 °C was used. Due to limited sensitivity of the detectors and higher liquid density, the experimental conditions under which the reliable pore diffusivity measurements can be provided are limited. Simulations have been carried out in order to analyze the effect of the model parameters and to choose the proper experimental conditions. The theoretical model which considers the ZLC cell as a continuous stirred tank has been applied. For both particle sizes, pore diffusivity at temperature of 25 °C is 4.0×10^{-6} cm^2/s and tortuosity 7 was calculated. Good agreement was found between the experimental and simulated desorption curves.

Keywords: Zero length column; Pore diffusivity; CHIRALPAK AD; Liquid chromatography; Mathematical modeling; Chiral alcohol

1. Introduction

Chromatographic methods are often used to characterize adsorption equilibrium and kinetic characteristic of the adsorbent. These methods have advantages in comparison with static or gravimetric methods, namely by elimination of external mass and heat transfer resistances [1–3]. On the other hand, when using chromatographic methods [4,5] one has to deal with axial dispersion. Therefore, the zero length column (ZLC) technique has been introduced to eliminate two major resistances in a chromatographic bed and to allow the measurement of pore diffusivity. The ZLC technique has been introduced by Eic and Ruthven [6] although in fact it is a shallow bed technique [7,8] used in the extreme situation of negligible film mass transfer resistance.

The technique is simple: at time zero the mobile phase flows through the shallow bed of ZLC previously saturated with a feed mixture at high flow rate and desorption curve is analyzed. The ZLC cell behaves as a continuous stirred tank and therefore the concentration at the surface of the particle can be related to the concentration on the outlet of ZLC cell [1,9,10]. This technique has been extensively used for the measurement of diffusivity of gases in zeolites. Extension for the liquid/solid system and the analytical solution has been made by Ruthven and Stapleton [11] and Brandani and Ruthven [12]. Recently, the zero length column method has been used for measurement of effective diffusion in ion exchangers [13–15]. However, there is no work about measurement of pore diffusivity in chiral adsorbents using ZLC technique. Chiral adsorbent CHIRALPAK AD coated on 20 and 50 μm silica gel substrate will be used as stationary phase for separation of racemate mixture of *S*,*R*-α-Tetralol. (*S*,*R*)-(±)-1,2,3,4-Tetrahydro-1-naphthol (*S*,*R*-α-Tetralol) is a secondary chiral alcohol and its enantiomer *R*-α-Tetralol is used as precursor for calcium antagonists commonly utilized in pharmacology and in drugs for the treatment of hypertension and angina pectoris [16–18]. Chiral Technologies Europe, France, supplied CHIRALPAK AD. The particles labeled 20 and 50 μm are in fact 27 and 49 μm, respectively. The basic physical-chemical properties are listed in Table 1 and the structural unit of chiral selector is shown in Fig. 1. This chiral selector is a chemically modified layer of amylose (amylose tris(3,5-dimethylphenyl carbamate)).

The objective of this work is to measure pore diffusivity of *R*,*S*-α-Tetralol enantiomers in chiral adsorbent CHIRALPAK AD with particle size 20 and 50 μm by using zero length column technique at temperature of 25 °C.

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Nomenclature

C_p	concentration of fluid phase in macropores (g/m^3)
C_0	initial concentration in the bulk fluid phase in the ZLC cell (g/m^3)
$\tilde{C}_p$	dimensionless macropore concentration
$\tilde{C}_0$	dimensionless concentration in the bulk fluid phase
D_m	molecular diffusivity (m^2/s)
D_p	diffusivity in macropores (m^2/s)
k_p	reciprocal diffusion time constant (1/s)
K	initial slope of isotherm [Henry constant]
K^*	capacity factor
L	ZLC operating parameter (Eq. (9))
M	molar mass (g/mol)
q	adsorbed phase concentration in equilibrium with C_p (g/m^3)
Q	purge flow rate (m^3/s)
R	radial coordinate in macropores (m)
R_p	particle radius (m)
V_m	molar volume of the adsorbate at its normal boiling temperature (m^3/mol)
V_{ZLC}	volume of shallow bed in ZLC cell (m^3)
t	time (s)
t_{inv}	inversion time (s)
T	temperature (K)

Greek symbols

β_n	roots of the transcendental equation (Eq. (15))
ε	void fraction of the ZLC
ε_p	particle porosity
ε_T	total porosity
ϕ	association factor
η	viscosity (Pa s)
τ	Tortuosity
τ_c	space time for ZLC (s)

Subscripts and superscripts

A, B	species in mobile phase mixture

Table 1
Physico-chemical properties of the chiral adsorbent CHIRALPAK AD [26][a]

Parameters	Specification
Appearance	White, off-white powder
Carbon content	14% ≤ C ≤ 16%
Loss on drying	Not more than 1.5 wt%

[a] Supplied by manufactures Chiral Technologies Europe.

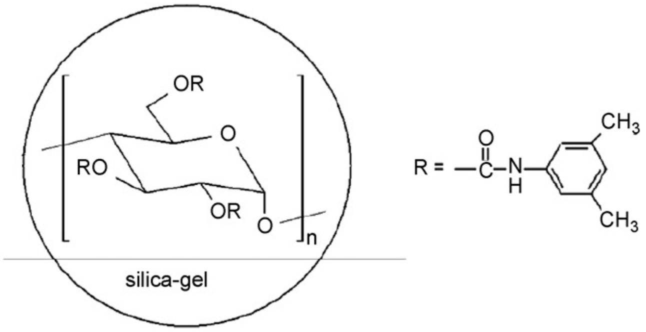

Fig. 1. The structural unit of the chiral adsorbent CHIRALPAK AD.

2. Theoretical

The mathematical model used to describe “zero length column” is based on the following assumptions:

- The adsorbent particle has porous structure and contain macropores.
- The particles have a spherical geometry and homogeneous size.
- The zero length column works as continuous stirred tank adsorber.
- Instantaneous equilibrium between the liquid phase in the macropore and solid phase.
- The adsorption equilibrium is linear.
- The film mass transfer resistance at the adsorbent external surface is negligible.

Model equations are as follows.

2.1. Overall adsorber mass balance in ZLC cell

$$V_{ZLC}\varepsilon \frac{dC}{dt} + QC + V_{ZLC}(1-\varepsilon)\frac{3}{R_p}D_p\varepsilon_p \left.\frac{\partial C_p}{\partial R}\right|_{R=R_p} = 0 \qquad (1)$$

where V_{ZLC} (cm^3) is the volume of the ZLC cell, C (g/dm^3) the bulk fluid phase concentration at the cell outlet, C_p (g/dm^3) the fluid phase concentration in the macropores, Q (cm^3/min) the purge flow rate, ε the cell porosity, ε_p the particle porosity and D_p (cm^2/s) is the macropore diffusivity, R (cm) the radial coordinate in the particle, R_p (cm) the radius of the particles and t (s) is the time.

The initial condition is given by:

$$t = 0; \quad C = C_0 \qquad (2)$$

where C_0 (g/dm^3) is the initial bulk fluid phase concentration.

2.2. Mass balance for the adsorbable component in the volume element of the particle

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \frac{\partial q}{\partial t} = \varepsilon_p D_p \left(\frac{\partial^2 C_p}{\partial R^2} + \frac{2}{R}\frac{\partial C_p}{\partial R}\right); \quad 0 \le R \le R_p,\ t > 0 \qquad (3)$$

where q (g/dm^3) is the adsorbed phase concentration per adsorbent volume.

The initial and boundary conditions are:

$$0 \le R \le R_p; \quad C_p(R,0) = C_0 \qquad (4)$$

$$t > 0; \quad \frac{\partial C_p}{\partial R}(0,t) = 0 \qquad (5)$$

$$t > 0; \quad C_p(R_p,t) = C(t) \qquad (6)$$