Journal of Chromatography A, 1294 (2013) 130–136

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

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

Determinations of gas–liquid partition coefficients using capillary chromatographic columns. Alkanols in squalane

Marcos Tascon, Lílian M. Romero, Agustín Acquaviva, Sonia Keunchkarian, Cecilia Castells *

Laboratorio de Separaciones Analíticas, División Química Analítica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, y CIDEPINT, 47 y 115 (1900) La Plata, Argentina

ARTICLE INFO

Article history:
Received 6 November 2012
Received in revised form 18 February 2013
Accepted 12 April 2013
Available online 18 April 2013

Keywords:
Gas–liquid partition coefficients
Squalane
Alkanols
Capillary columns
Interfacial adsorption

ABSTRACT

This study focused on an investigation into the experimental quantities inherent in the determination of partition coefficients from gas–liquid chromatographic measurements through the use of capillary columns. We prepared several squalane – (2,6,10,15,19,23-hexamethyltetracosane) – containing columns with very precisely known phase ratios and determined solute retention and hold-up times at 30, 40, 50 and 60 °C. We calculated infinite dilution partition coefficients from the slopes of the linear regression of retention factors as a function of the reciprocal of the phase ratio by means of fundamental chromatographic equations. In order to minimize gas–solid and liquid–solid interface contributions to retention, the surface of the capillary inner wall was pretreated to guarantee a uniform coat of stationary phase. The validity of the proposed approach was first tested by estimating the partition coefficients of n-alkanes between n-pentane and n-nonane, for which compounds data from the literature were available. Then partition coefficients of sixteen aliphatic alcohols in squalane were determined at those four temperatures. We deliberately chose these highly challenging systems: alcohols in the reference paraffinic stationary phase. These solutes exhibited adsorption in the gas–liquid interface that contributed to retention. The corresponding adsorption constant values were estimated. We fully discuss here the uncertainties associated with each experimental measurement and how these fundamental determinations can be performed precisely by circumventing the main drawbacks.

The proposed strategy is reliable and much simpler than the classical chromatographic method employing packed columns.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Dynamic gas–liquid chromatography (GLC) is an established method for determining relevant thermodynamic quantities including infinite dilution activity coefficients and gas–liquid partition coefficients (K_L) of volatile compounds in nonvolatile solvents [1,2].

Since GLC's inception, the chromatographic measurements of K_L have mainly been carried out by using packed columns. Although almost all separations today are performed with capillary columns, the use of that format for physicochemical measurements has been quite limited [3–5] for two principal reasons. First, several solvents of interest cannot be immobilized onto the inner walls of the capillary; second, chromatographers are used to calculating partition coefficients from the measurement of solute net or specific retention volumes. These quantities are derived from the measurements of flow-rate, which determination is not accurate when wall-coated columns are used because of the difficulties in reliably measuring very small volumetric flow-rates.

Nonetheless, infinite dilution partition coefficients can be directly calculated from retention times, without conversion to retention volumes, provided that the column phase ratio (β) is known. When capillary columns prepared by the static method are used, β can be exactly calculated at any temperature from a knowledge of the conditions used to fill the capillary tubes in addition to the liquid phase density at the same temperature [6]. The main advantage of a capillary column lies in the simplicity of its geometry and the inertness of the inner capillary after a proper pretreatment as compared to any porous and thus tortuous, support used to prepare packed columns. A simple estimation of the solid surface for a 10-m × 250-μm i.d. capillary tube gives an inner area as low as 0.008 m^2. In contrast, any packed column of normal dimensions has an area of more than 1–2 m^2. This difference of more than 2 orders of magnitude implies a significant reduction of the possibilities for adsorption onto gas– and liquid–solid interfaces. Moreover, since peaks eluted from capillary columns

* Corresponding author. Tel.: +54 221 4228328; fax: +54 221 4271537.
E-mail address: castells@isis.unlp.edu.ar (C. Castells).

0021-9673/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chroma.2013.04.032

are significantly narrower, their maximum position is more distinctly defined. In addition, narrower peaks are necessarily taller, and thus much smaller injection amounts are required for obtaining a measurable signal.

In principle, the possibility of adsorbing the solute onto the solid surface (packing support or the silica wall) or onto the gas–liquid interface should be considered. This question is of special concern when a large surface is available [7–10]. If adsorption in a given interface occurs, the retention volumes will be the result of both partition and adsorption. In this circumstance, skewed peak profiles are commonly observed [3,11–13]. Zhang et al. [3] discussed different methods to measure K_L when peaks are asymmetric and reached to the conclusion that a diminution in the adsorption effects is necessary in order to acquire accurate measurements of K_L.

The first condition to be fulfilled for obtaining symmetric peaks is the injection of a sample amount within the infinite dilution region for all the sorption phenomena. The observation of symmetrical peaks, however, indicates that infinite dilution has been attained for all the sorption processes, but not that adsorption effects are absent, and therefore, even when symmetric peaks are observed, potential interfacial effects may still exist.

The aim of the present work was to discuss how capillary columns of exactly measured phase ratios can be used to determine gas–liquid partition coefficients, even when significant gas–liquid interfacial adsorption is present. Thus, we determined the partitioning of aliphatic alcohols in a typical nonpolar stationary phase, such as squalane, with wall-coated columns. This was a challenging system to test the suitability of capillary columns in obtaining accurate solution thermodynamic data, since gas–liquid interface adsorption concurrent with the partitioning process must be taken into account.

2. Theory

For a solute i distributed between liquid and vapor phases, the equilibrium condition is given by the equality of the fugacities in both phases or, at moderate pressures:

$$y_i P = \gamma_i x_i P_i^o \tag{1}$$

where y_i and x_i are the solute molar fractions in the gas and liquid phases, respectively, γ_i is the solute liquid-phase activity coefficient in the molar fraction scale, P is the total pressure, P_i^o is the solute saturated vapor pressure at temperature T. In Eq. (1), the interactions of the solute molecules with the carrier-gas molecules can be considered negligible in open tube GLC measurements at low gas inlet pressure [14,15]. At pressures affording ideal gas behavior, the partial pressure of the solute is related to the concentration of solute in the gas phase, C_i^g. Thus, the left-hand side of Eq. (1) can be equaled to

$$y_i P = C_i^g RT \tag{2}$$

Similarly, at $x_i \to 0$, the right-hand side of Eq. (1) can be written as

$$\gamma_i x_i P_i^o = \gamma_i^\infty C_i^L v^l P_i^0 \tag{3}$$

where γ_i^∞ is the solute infinite dilution activity coefficient, v^l is the liquid molar volume and C_i^L is the molar concentration of solute i in the liquid. The infinite dilution partition coefficient K_L, defined as the ratio between C_i^L and C_i^g is easily obtained from Eqs. (2) and (3):

$$K_L = \frac{C_i^L}{C_i^g} = \frac{RT}{P_i^0 \gamma_i^\infty v^l} \tag{4}$$

Several methods to measure either K_L or γ_i^∞ data have been proposed, with the most widely used being GLC. In a chromatographic gas–liquid system, the solute retention volume is mainly a result of the partition process. Other retention mechanisms, however, are also known to take place. These additional simultaneous processes are mainly owing to strong interactions of certain solutes at gas–liquid (GL), solid–liquid (SL) and gas–solid (GS) interfaces of any system. Thus, solute retention in the presence of these concurrent distribution processes is described by [7,8,16]:

$$V_N = K_L V_L + K_A A_L + K_I A_I + K_S A_S \tag{5}$$

where V_N represents the net retention volume, V_L is the stationary phase volume, A_L, A_I, A_S represent the surface areas of the GL, SL and GS interfaces, respectively; and K_A, K_I and K_S are the adsorption isotherm slopes of the three above-mentioned processes. Whenever thoroughly deactivated solid supports are used with highly loaded columns, the last two terms in Eq. (5) can be ignored, so that:

$$V_N \cong K_L V_L + K_A A_L \tag{6}$$

Traditionally, K_L is estimated from the intercept of plots V_N/V_L against $1/V_L$, using a set of packed columns with different stationary phase loadings.

Since:

$$\frac{V_N}{V_M} = \frac{t_R}{t_M} - 1 = k \tag{7}$$

in which equation, t_R and t_M are retention time for the solute as well as a for a nonretained analyte, respectively, k denotes the solute retention factor, and V_M the hold-up volume, the following expression can be written by combining with Eq. (6):

$$\frac{t_R}{t_M} - 1 = K_L \left(\frac{V_L}{V_M}\right) + K_A \left(\frac{A_L}{V_M}\right) \tag{8}$$

where the ratio (V_L/V_M) is the reciprocal of the column phase ratio, β.

3. Experimental

3.1. Instrumentation and materials

Chromatographic measurements were performed in an HP6890 (Agilent) gas chromatograph equipped with flame-ionization detection and manual-injection port. The data were acquired by means of the software Clarity (DataApex, Czech Republic).

Fused silica capillary tubing of 250 μm i.d., provided by MicroQuartz (München, Germany), was used to construct the chromatographic columns. Carbowax 20M was obtained from Alltech (Alltech, Deerfield, IL, USA) and the solvents from Merck KGaA (Darmstadt, Germany). The squalane (HP, Avondale, PA, USA) was used as received; solutions in dichloromethane, at the concentrations given in Table 1, were prepared avoiding air contact to prevent oxidation [21]. The density of squalane within the same temperature interval had been measured previously by pycnometry [9]. Data had been fitted to the equation ρ_s $(g\,cm^{-1}) = 0.8195(\pm 5 \times 10^{-4}) - 6.0899(\pm 1 \times 10^{-5}) \times 10^{-4} t$, where t is the temperature expressed in °C.

All the solutes were analytical-reagent grade and they were used as received from the supplier. Solutes were contained in 2.5-mL vials with a valve cap, and kept at room temperature, and injected with Hamilton syringes at least three times. Four temperatures, in the 30–60 °C range, were used. Retention times were measured at the peak maximum with a precision of 0.001 min. The extracolumn volume was negligible for the column dimensions used in this work.

Download English Version:

https://daneshyari.com/en/article/1201018

Download Persian Version:

https://daneshyari.com/article/1201018

Daneshyari.com