Characterisation of stationary phases in subcritical fluid chromatography with the solvation parameter model III. Polar stationary phases

C. West, E. Lesellier *

LETIAM, Groupe de Chimie Analytique de Paris Sud (EA 3343), IUT d'Orsay, Plateau du Moulon, 91400 Orsay, France

Abstract

In this third paper, varied types of polar stationary phases, namely silica gel (SI), cyano (CN)- and amino-propyl (NH2)-bonded silica, propanediol-bonded silica (DIOL), poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA), were investigated in subcritical fluid mobile phase. This study was performed to provide a greater knowledge of the properties of these phases in SFC, and to allow a more rapid and efficient choice of polar stationary phase in regard of the chemical nature of the solutes to be separated. The effect of the nature of the stationary phase on interactions between solute and stationary phases and between solute and carbon dioxide-modifier mobile phases was studied by the use of a linear solvation energy relationship (LSER), the solvation parameter model. The retention behaviour observed with sub/supercritical fluid with carbon dioxide–methanol is close to the one reported in normal-phase liquid chromatography with hexane. The hydrogen bond acidity and basicity, and the polarity/polarizability favour the solute retention when the molar volume of the solute reduces it. As with non-polar phases, the absence of water in the subcritical fluid allows the solute/stationary phase interactions to play a greater part in the retention behaviour. As expected, the DIOL phase and the bare silica display a similar behaviour towards acidic and basic solutes, when interactions with basic compounds are lower with the NH2 phase. On the CN phase, all interactions (hydrogen bonding, dipole–dipole and charge transfer) have a nearly equivalent weight on the retention. The polymeric phases, PEG and PVA, provide the most accurate models, possibly due to their better surface homogeneity.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Stationary phases; Subcritical fluid chromatography; Solvation parameter model; Linear solvation energy relationship; Silica; Amino; Cyano; Diol; PEG; PVA

1. Introduction

In packed column supercritical fluid chromatography (SFC), the choice of the chromatographic system (stationary phase and mobile phase) that will be the most appropriate to separate a given mixture of solutes is a complex problem. One of the reasons for this difficulty is the great diversity of available stationary and mobile phases as most solvents are miscible to carbon dioxide (apart from the very polar ones, as water), and all packed columns available for high-performance liquid chromatography (HPLC) can be used with supercritical fluids as well.

In this context, the classical process of method development is to use several different columns (most often 4–6 different types of stationary phases) and several different modifiers associated to carbon dioxide as the mobile phase, and to test all combinations in a preferential order based on the operator's experience. Then, the stationary–mobile phase combination inducing the best result is selected and an optimisation process based on the modification of all other experimental conditions (such as temperature, pressure and possibly elution gradients) generally allows to reach a satisfying separation.

Unfortunately, these vast possibilities are generally associated to a lack of knowledge of the interactions occurring between the solutes, the stationary phase and the mobile phase. Thus, apart from the very common octadecyl-bonded silica (ODS) and silica gel stationary phases, the potential of a chromatographic system for a given separation is generally not well evaluated. This is particularly true for polar-bonded stationary phases as the understanding of the retention mechanisms occurring on these phases is still too limited to offer an alternative to trial-and-error procedures when selecting a stationary phase. Indeed,

polar-bonded silica stationary phases are widely used in SFC (see for example [1–9]). However, as far as we know, no global study comparing the properties of the different bonding types was ever published. Besides, the notion of "polarity" (of the solutes, the stationary or the mobile phase), generally determining the initial choice of the chromatographic system, is a relative notion, based on the experience of the operator.

An understanding of the processes that govern retention will permit prudent selection of the stationary and mobile phases that will be the most appropriate for a specific application. Stationary phase selection should be based on first characterizing the capacity of the stationary phase for specific intermolecular interactions and then using this information to predict solute retention.

Quantitative structure–retention relationship (QSRR) allows the extraction of precise information from large amounts of retention data [10–12]. One of the most used QSRR for the description of chromatographic systems is the solvation parameter model based on Abraham solute descriptors [11,12]:

$$\log k = c + eE + sS + aA + bB + vV. \tag{1}$$

In this equation, capital letters represent the solute descriptors, related to particular interaction properties, while lower case letters represent the system constants, related to the complimentary effect of the phases on these interactions. c is a constant, depending on specific column parameters such as porosity. E is the excess molar refraction (calculated from the refractive index of the molecule) and models polarizability contributions from n and π electrons; S is the solute dipolarity/polarizability; A and B are the solute overall hydrogen-bond acidity and basicity; V is the McGowan characteristic volume in units of $cm^3\,mol^{-1}/100$. The system constants (c, e, s, a, b, v), obtained through a multilinear regression of the retention data for a certain number of solutes with known descriptors, reflect the magnitude of difference for that particular property between the mobile and stationary phases.

The solvation parameter model was used with polar-bonded phases in HPLC, in reversed-phase (RP) and in normal-phase (NP) modes. In reversed-phase mode, for propanediol- and cyanopropyl-bonded stationary phases, the coefficients ruling the retention are v (positive) and b (negative) [13–15]. These results could appear surprising as this would mean that an increase in the hydrocarbonaceous volume V would induce an increase in retention on polar stationary phases, while an increase in the hydrogen-bond accepting ability of the solute (B) would cause a decrease in retention. However, the same behaviour is obtained with ODS stationary phases, underlining that the acidity and cohesiveness of water are the most important properties acting on retention, when an aqueous mobile phase is used, whatever the polarity of the stationary phase. Therefore, in the reversed-phase mode, the polarity of the diol and cyano phases cannot be used to achieve separations on the basis of polar interactions between solutes and the stationary phase.

For both stationary phase types, polar and non-polar, the decrease in the water content in the mobile phase dramatically reduces the v and b values, whatever the organic solvent associated to water (methanol, acetonitrile, tetrahydrofuran, or isopropanol) [13,16]. However, the values of the other coefficients (e, s and a) does not vary significantly. Judging by the dominant role played by water in RP separations, the studies performed in aqueous mobile phases thereby provide little insight into the retention mechanism for SFC.

Other studies were done in NP-HPLC mode, on diol, cyano, amino and silica gel stationary phases [17–21]. Whatever the stationary phase, the results are opposite to those obtained in the RP mode. v becomes negative, showing that the increase in the volume of the compounds decreases the retention, when a, b and s become positive, showing that dipole–dipole and hydrogen-bond interactions favour the retention. In pure hexane, the acidity of diol and amino-bonded phases is greater than the one of the cyano phase, but the addition of a 1% of methanol in hexane strongly changes the model coefficients, on all tested phases [12].

Amongst the LSER studies of polar phases, some were performed in SFC with cyano phases [22,23]. However, the equations used in these studies do not allow a clear comparison between SFC and HPLC, because the term describing the dispersive interactions and the cavity energy was different.

Indeed, for processes occurring between a condensed phase and a gaseous phase, another equation is used where the V descriptor is replaced by L, the partition coefficient of the solute from the gas phase to *n*-hexadecane at 298 K. In supercritical fluids, there is no general agreement whether V or L should be preferred. Depending on the density of the fluid used, some authors choose to use the L descriptor [22–26], while others choose the V descriptor [27–32]. As these are not interchangeable, comparisons between results obtained with the one or the other are difficult.

In the first two papers, we compared varied alkyl-bonded silica stationary phases, investigating the effect of varied lengths of the alkyl chain, embedded groups and fluoroalkyl bonding [33,34].

In this third paper, we will present a detailed study of polar stationary phases, investigating the effect of varied polar-bonded groups and polymers, compared to bare silica gel, by using the classical LSER equation and the same mobile phase. The properties of the stationary phases will be compared using some tools introduced in the second paper of this series [34], namely the solvation vectors associated to the chromatographic systems characterized by the LSER method.

The phases studied comprise silica gel (SI), polar-bonded silica such as cyanopropyl-bonded silica (CN), propanediol-bonded silica (DIOL), and aminopropyl-bonded silica (NH2), and polymers such as poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA).

2. Experimental

2.1. Stationary phases

All the stationary phases used in this study are commercially available and were kindly offered by the manufacturers. The names and known properties of the columns used are presented in Table 1. The nature of the bonding is represented on Fig. 1. The particle platform of the PEG and PVA phases is silica.