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Study of dead volume measurement in packed subcritical fluid chromatography with ODS columns and carbon dioxide–modifier mobile phases

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Abstract

Studies were done for providing a simple, rapid and reliable procedure of void volume measurement in packed subcritical fluid chromatography (pSubFC), with CO_2–modifier mobile phases containing high modifier amounts. Methods used in RPLC with ODS columns were applied in pSubFC: gravimetric, homologous series linearisation and unretained marker injection. Results lead us to propose the method of marker injection to determine the void volume in pSubFC. Acetonitrile was chosen as the void volume marker among six tested markers. Furthermore, void volume variations vs. the modifier volume (from 5 to 45%) were studied for nine organic modifiers. The void volume variations were related both to adsorption–desorption phenomena between the mobile phase and the stationary phase and to mobile phase density changes. These variations allowed the classification of the modifiers into four groups on the basis of the molecular interactions.

Keywords: Void volume; Carbon dioxide; Methanol; Acetonitrile; Subcritical fluid chromatography

1. Introduction

The study of molecular interaction mechanisms (distribution or adsorption mechanism) or the achievement of an eluotropic strength scale with chromatographic analyses requires the calculation of two parameters at least, retention factor (k) and selectivity (α). Retention factor k represents the sum of different molecular interactions that take place in the column. These interactions bring the solute–mobile phase, solute–stationary phase and mobile phase–stationary phase relationships into play. Obviously, the calculation of parameters, k and α, involves a perfect knowledge of dead volume (V_0) or of dead time (t_0).

The methods allowing void volume measurement depend on chemical nature of the stationary phase (pure or bonded silica), on the physical state of the mobile phase (liquid or gazeous), or on the type of column (capillary or packed). Four methodologies were used: calculation, gravimetry, linearisation of homologous series and injection of unretained markers.

With neat carbon dioxide, the dead volume of the column was calculated as a reduced parameter from the densities of crystalline state and from the chro-

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matographic conditions [1]. For CO_2-modifier mobile phases, it was estimated from both the pore and interstitial volumes [2]. A gravimetric method was also used [3]. The column was filled with pure CO_2, then it was depressurised and was left opened to atmosphere until to reach a stable mass. The column was weighed, then it was filled with methanol and reweighed. The difference between the two masses allowed calculation of column porosity.

However, these two first methods are static ones. The estimated void volume is unvariable whatever the analytical conditions, which leads to ignoring some phenomena like mobile phase adsorption onto stationary phase or mobile phase compressibility.

The linearisation of homologous series was successfully used with reversed-phase liquid chromatography (RPLC) [4]. It is based on the concept that a linear relationship exists between log k and carbon atom number (C_n) of the members of the homologous series [5]. Because the increase in the retention time follows regularly the increase in the hydrocarboneous volume of the solutes [6–9], the retention behavior in sub or supercritical fluid chromatography using ODS stationary phase is similar to the one observed in reversed-phase chromatography, especially when polar modifiers are added to the carbon dioxide from 5 to 45% [7–9]. Moreover, because this retention behavior is also observed at 10°C [9], it is rather due to solubility changes, as observed in RPLC, than to compound volatility [10]. That explains why the linearisation of homologous series was used in packed supercritical fluid chromatography (pSFC) [11]. From this linearisation method, an iterative procedure was carried out [12] and applied in capillary supercritical fluid chromatography (cSFC) with carbon dioxide and butane [13].

Whatever the type of chromatography, unretained marker injection is probably the most used method. The difficulty is to select an unretained compound. Due to the apolar character of supercritical carbon dioxide, saline solutions or uracil cannot be injected in SFC. Gases were mainly injected in cSFC [13,14] but also in pSFC [15]. With neat carbon dioxide, methane was detected with a flame ionisation detector [14,15] when helium was detected by a UV spectrophotometer [13]. Because helium has no affinity for the stationary phase, it can be an accurate hold-up time marker [13,16]. Neon and argon were also used as void volume markers, in studies achieved in mass spectrometric tracer pulse chromatography [17–19].

This method requires a gas-sampling valve pressurised to inject a gaseous mixture of isotopically labeled fluids in the same composition to the one of the mobile phases, and a mass spectrometer detector as a mass specific one [17]. With neat CO_2, the relationship between void volume variations and adsorbed amount of CO_2 shows that neon was not soluble in the adsorbed phase [18].

Unfortunately, the slight solubility of neon in methanol–CO_2 mixtures requires a correction of the void volume which increases the difficulties of this method [19]. Moreover, the injection of a gaseous mixture (CO_2–modifier) with a high modifier percentage (up to 45%) seems to be difficult.

Organic solvents were also tested for dead volume measurements in pSFC. Hexane, benzene and carbon tetrachloride were shown to exhibit some degree of retention even at high pressure [20]. Acetone and methylene chloride peaks were taken as a measure of the dead time column [7,21–23], even with high modifier percentage in the mobile phase [21]. On ODS column, methylene chloride was unretained with neat CO_2, only if the pressure was higher than 15 MPa [23]. With alcohol as modifier, water can be used as an unretained compound [24]. However, in numerous conditions, the marker injection leads to overestimation of the void volume [13].

The aim of this work is to provide a simple procedure for measuring dead volume in pSubFC with ODS columns and high modifier amount mixed to the carbon dioxide. Two methods able to measure the void volume changes were tested: linearisation of the homologous series retention and marker injection. Finally, relationships between the dead-volume variations and organic-modifier nature or percentage were studied and related to the physical and chemical phenomena taking place in the column.

2. Experimental section

2.1. Chromatographic system

The chromatographic system was a Gilson SF3 system (Villers le Bel, France). Carbon dioxide was

pumped with a Gilson Model 308 pump. The pump head was thermostated to −6°C with a cryostat (Huber, Offenburg-Elgersweiser, Germany). Modifier was pumped with a Gilson Model 306 pump. Mixing took place in a Gilson Model 811C dynamic mixer with a 1.5 ml mixing chamber. The column was thermostated with an oven Croco-cil (Cluzeau, Ste Foix la Grande, France). The Rheodyne injection valve had a 20 μl loop (Cotati CA, USA). Detection was accomplished using a Gilson Model 119 variable wavelength UV/visible detector with a 7 μl high pressure flow cell (30 MPa). Column backpressure was maintained using a Gilson Model 821 pressure regulator. Chromatograms were plotted on a Shimadzu integrator, model C-R6A (Kyoto, Japan, supplied by Touzart et Matignon, Les Ulis, France). The analyses for the research of wavelength detection were carried out with a Jasco MD 910 diode array detector (Tokyo, Japan supplied by Prolabo, Fontenay sous bois, France). Verification of the visible wavelength ability to detect the solvent peak was done with a UV/visible Hewlett-Packard detector (HP 1050).

2.2. Columns

Two monomeric octadecyl bonded silicas were used: Kromasil C18 (250 mm, 4.6 mm, 5 μm) (Eka Nobel, Bohus Sweden) and Hypersil ODS (250 mm, 4.6 mm, 5 μm) (Hypersil, Runcorn, UK). The main differences between these two stationary phases were the greater specific area of the silica and the higher density of the bonded silica for the Kromasil C18 column.

2.3. Chemicals

SFC grade carbon dioxide was purchased from l'Air Liquide (Vitry sur Seine, France). HPLC grade organic solvents were: acetonitrile (Merck, Darmstat, Germany), tetrahydrofuran, acetone and heptane (SDS, Peypin, France), methanol (Carlo Erba, Rodano, Italy), ethanol (Prolabo, Fontenay sous bois, France). The homologous series was the alkylbenzene series (Aldrich, St Louis Missouri, USA), from $C_n=1$ (toluene) to $C_n=19$.

2.4. Chromatographic conditions

The flow rate was 3 ml min^{-1}. The analysis temperature was 20°C. Column backpressure was 10 MPa. Columns were put in series for the study about linearisation of homologous series retention. This column length increase facilitates the determination of the retention time of weakly retained homologues, i.e. those having a short chain length. The relative standard deviation on the void volume was calculated from six injections and was equal to 0.2%.

3. Results and discussion

3.1. Dead-volume measurements with the method of linearisation of homologous series retention

The determination of V_0 is based on the linearity of $\log k = f(C_n)$ curves. The method applied in this study is an iterative procedure, as the retention factor of each homologue compound is calculated with several V_0 values [25]. The selected V_0 value enables to obtain the best linearisation of the curves $\log k = f(C_n)$. According to Laub, this best V_0 value is reached when the correlation coefficient R^2 of the previous relation is maximum [26]. Due to the great eluotropic strength of carbon dioxide, the retention time of solutes is often smaller in SubFC than in HPLC. That increases the difficulty of measuring retention times. Four Hypersil columns were connected to improve the accuracy of these measurements.

For the linearisation study, tested V_0 values ranged from 8 to 12 ml, which correspond to porosities from 0.48 to 0.72 with a geometric volume equal to 16.62 ml.

Alkylbenzenes were used for the linearisation, because they can be detected with the UV/visible detector with CO_2/modifier mobile phases. Furthermore, no difference was reported between methylene selectivity measured from the longest homologues of alkylbenzene series and from three other series [9].

However, whatever the homologous series used, subtle changes in the retention mechanisms, that occur when the homologous compound chain length increases, are able to slightly modify the linearity of the previous relationship [27,28]. Because these

changes are often undetected using few homologues, 19 compounds were chromatographied in this study. As the retention behavior of the small homologues can depend on the size and on the polarity of the polar head [27,29], the iterative procedure was performed either with all the compounds of the homologous series or only with $C_n > 8$ (Fig. 1). This lower limit value ($C_n > 8$) was chosen to be higher than usual ($C_n = 6$) [30]. Whatever the homologue number (11 or 19), correlation coefficients R^2 obtained were excellent (0.99999 from the eleven longest homologues and 0.99985 from all the series). This underlines that the contribution of an additional methylene group increases the retention, as it is usually reported in RPLC mode. However, the selected V_0 value varies as a function of the homologous compound number used. Following the number of homologues used for the linearisation, V_0 is equal to 10.71 ml or to 9.81 ml, corresponding to a porosity equal to 0.64 and to 0.59. The explanation of the observed void volume difference is that the interaction mechanisms between solutes and stationary phase can slightly change according to the carbon atom number of the homologous compounds [28]. Moreover, the curves $\alpha = f(C_n)$, determined from the retention factor calculated for all the homologues with these two dead volume values cannot be described with the same mathematical model. The choice to use one or other V_0 value leads to selecting the selectivity curve shapes and the retention mechanisms. This method of measurement was not retained.

3.2. Measurement of dead volume with marker injection

3.2.1. Choice of the marker

Dead volume is calculated with the equation $V_0 = t_0 f$ where f is the flow-rate. Two Hypersil columns were used for this study (geometric volume, $V_g = 8.31$ ml). The choice of the selected marker was done following two criteria about the signal obtained after marker injection. The first criterion is a sufficiently intense response for an easier measurement of

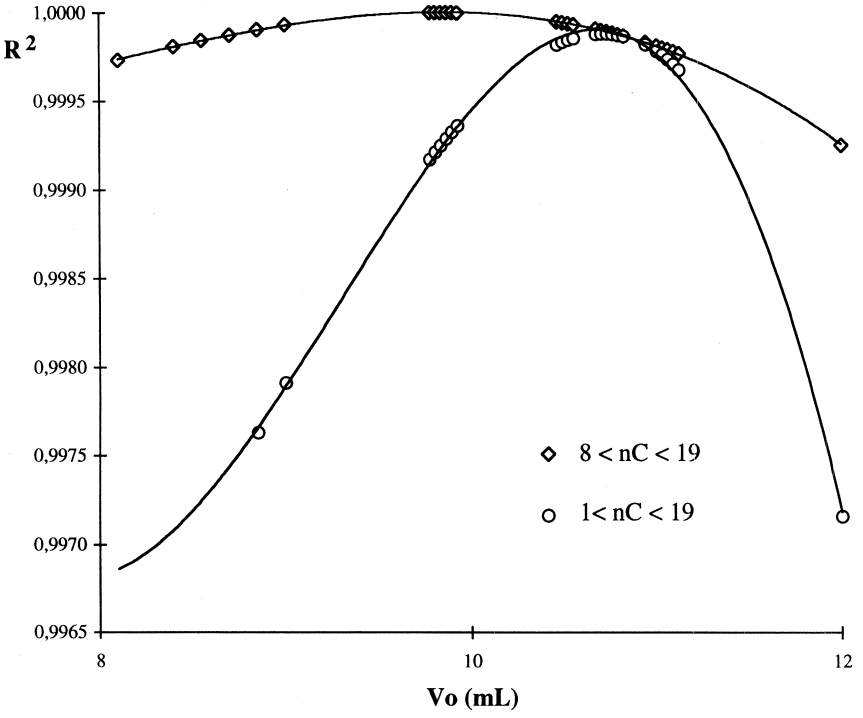

Fig. 1. Correlation coefficient (R^2) calculated with different $V_{0\ app}$. Homologous series: alkylbenzenes ($C_n = 1$ to $C_n = 19$. Columns: four Hypersil ODS. Mobile phase: CO_2–ACN, 90:10 (v/v). $T = 20$°C, $P_{outlet} = 10$ MPa, flow-rate = 3 ml min^{-1}, detection wavelength: 210 nm.

retention time and the second one is the non-retention of the injected marker.

Because the first studies were achieved with a polar modifier (acetonitrile) water was injected, because it does not interact with the apolar octadecyl chains of the stationary phase. Unfortunately, the water signal intensity was very low, which prevents the use of this compound as a dead volume marker.

All markers commonly used in RPLC were injected: acetonitrile, acetone, methanol and tetrahydrofuran. Heptane, which has a cut off equal to 197 nm, was also injected to compare its behavior between SubFc and SFC.

The signal obtained at 195 and 210 nm for organic markers is presented in Fig. 2, while a CO_2–acetonitrile mobile phase was employed.

All markers give chromatograms with two signals. The first signal is positive (tetrahydrofuran) or negative (acetonitrile, methanol, acetone). The second signal is always positive. Because the intensity of this second peak increases strongly when the wavelength decreases from 210 to 195 nm, it corresponds to the injected species. Among the injected markers, tetrahydrofuran, heptane and methanol are the more strongly retained into the column. This result emphasises the strong affinity of the alkane for octadecyl bonded chains, even if polar modifier is added to the carbon dioxide. The methanol peak is asymmetrical, that underlines, when using an ODS column, secondary interactions, mainly with residual silanols.

The negative spikes observed for acetonitrile, methanol and acetone appear at a shorter time than the one for the first perturbation of tetrahydrofuran and heptane. Moreover, the time of this first perturbation is the same for methanol, acetone and acetonitrile. This result shows that this negative deviation is independent of the injected marker nature, and due to the passing across the detector of injected molecules leaving the column first. Another study performed in SFC with silica columns has also shown two peaks, whatever the modifier nature and its percentage in the mobile phase [31]. This first one, positive in this case, always appeared before the solvent peak, as the negative peak in our study.

Among these three solvents, acetonitrile was chosen as dead volume marker because its negative spike is the most intense (Fig. 2), which was required by the first criterion. The retention time of this negative peak is equal to 1.88 min, and the corresponding V_0 is 5.64 ml. The porosity determined from this value is 0.67.

According to previous study carried out in HPLC with a refractometric injector by the injectiojn of deuterated species [32], the chromatographic peaks obtained in SFC can be explained by a series of equilibria in the mobile phase, leading to the observed chromatograms. After these equilibria, the injection band arrives in the detector. The signal shows one negative peak. Because pure acetonitrile (injection without a column) provides positive peak, the negative spike could be due to an excess of CO_2 in this injection band, in comparison to the mobile phase composition.

However, with a UV/visible spectrophotometric detector, it is difficult to assert that the first negative deviation is really due to an absorption variation. Moreover, no variation of the first negative perturbation shape appears when the detection wavelength changes (between 195 and 210 nm). This first negative peak seems be due to a difference between the refractive index of the mobile phase and that of the injection band. This kind of unexpected behavior of UV detector was also reported for V_0 measurements, by the production of a negative spike on the baseline due to the passing of helium [13].

Finally, one can note that an additional little positive peak follows the first negative one (Fig. 2). This is a compensation peak, well known in RPLC, and also due to a refractive index variation. To simplify the measurement, we have decided to use the time on the negative peak maximum for determining the dead volume, because the time difference between these two peaks was negligible.

3.2.2. Choice of detection wavelength

A study of the effect of modifier percentage on the measured dead volume values was performed (from 5 to 45%), by using one Kromasil column, with injection of pure acetonitrile. Modifier nature varied from pure ACN to pure methanol, with different ACN–methanol mixtures (Fig. 3). The percentages of modifier-mixtures are regularly spaced for better describing the evolution of the dead volume.

The results show that the measured V_0 varies with organic-modifier nature. The variations observed will

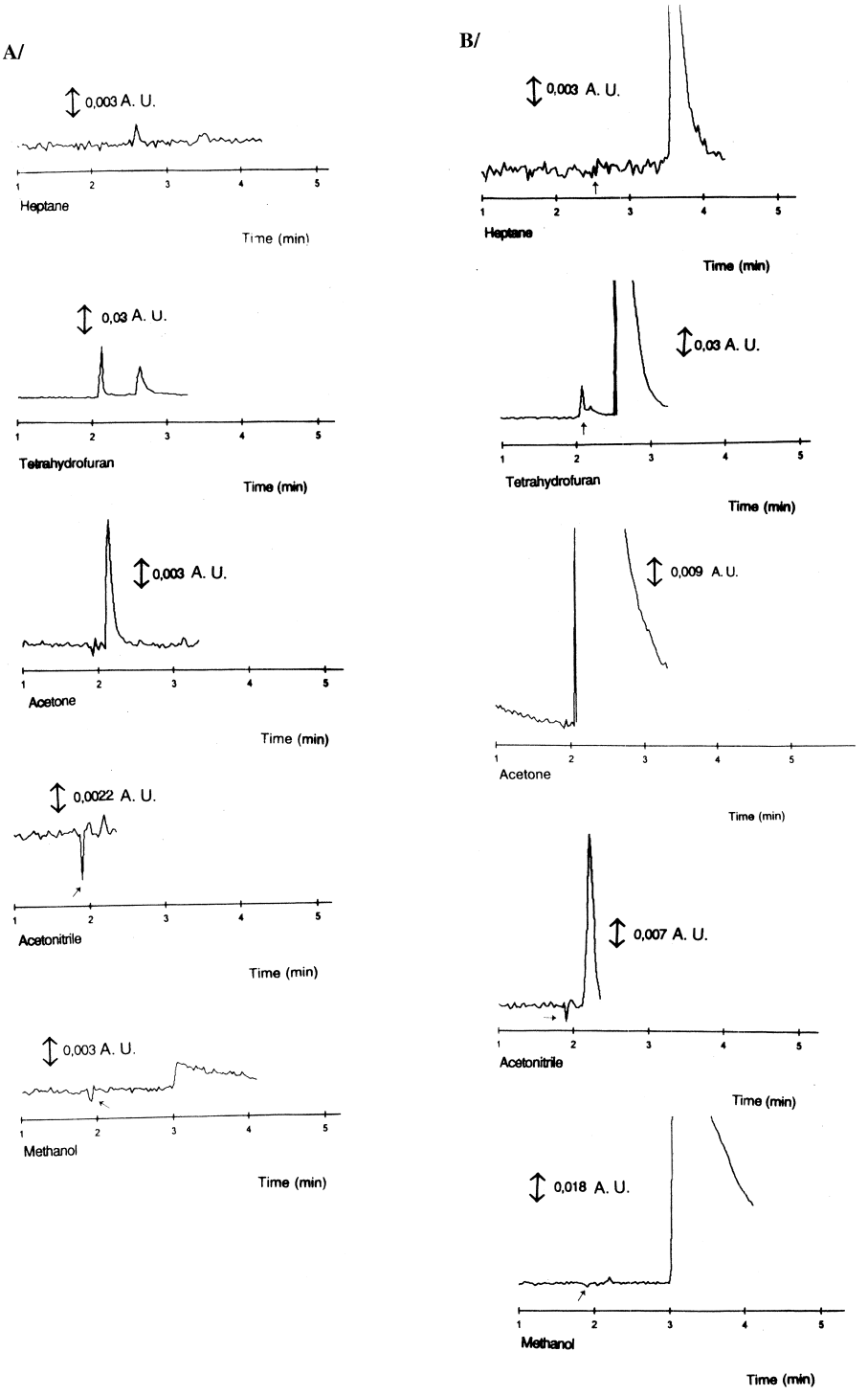

Fig. 2. Chromatograms of different injected organic solvents. A/210 nm; B/195 nm. Columns: two Hypersil ODS. Mobile phase: CO_2–ACN, 90:10 (v/v). $T=20°C$, $P_{outlet}=10$ MPa, flow-rate=3 ml min^{-1}.

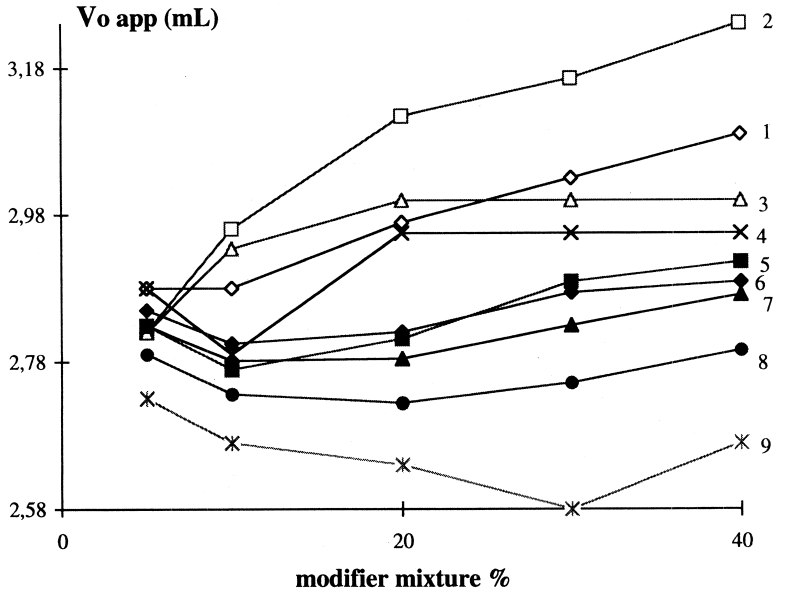

Fig. 3. $V_{0\ app}$ variations vs. ACN–MeOH modifier mixture percentages in CO_2 at 210 nm. **1**. neat ACN. **2**. 90:10 (v/v). **3**. 80:20 (v/v). **4**. 70:30 (v/v). **5**. 40:60 (v/v). **6**. 30:70 (v/v). **7**. 20:80 (v/v). **8**. 10:70 (v/v). **9**. neat MeOH. Column: one Kromasil C18. $T=20°C$, $P_{outlet}=10$ MPa, flow-rate=3 ml min^{-1}.

be discussed in the next paragraph. For methanol-rich modifier mixtures, V_0 evolution is regular: V_0 decreases when methanol percentage increases. However, some irregularities appear for ACN-rich modifier mixtures. The dead volume measured with ACN–methanol modifier mixture, in a proportion of 90:10, is higher than the ones measured with ACN–methanol modifier mixture in a proportion of 80:20.

This problem is due to the difficult measurement of the first deviation at 210 nm, because the perturbation shape varies with modifier mixture percentage in the mobile phase. This shape passes from a simple appearance with two peaks to a more complex appearance. To avoid this phenomenon which occurs in the UV range, the study of the variation of the first deviation appearance in the visible range was carried out with a diode array detector. The visible range was chosen because previous studies on separation of carotenoid, which has an absorption maximum at 450 nm [3], have shown the possible use of this visible wavelength to measure the void volume.

As expected, the dead volume signal is always present on the chromatogram in the visible wavelengths. Moreover, no variations of signal appearance can be described at these wavelengths.

However, because acetonitrile does not possess chromophore group, this peak is probably due to a refractive index variation modifying the light which falls on the photodiodes. Because this deviation was obtained using three different detectors in the visible range, the signal perturbation is not specific to one detector but a more general phenomenon. Moreover, other study using a modified UV detector (Jasco 970-UV) in SFC, has shown the ability of this UV detector to detect the methylene chloride peak at 600 nm, even with a lack of chromophore group. Authors have also attributed this detector response to a refractive index change caused by the injected solvent [33].

A study was carried out with all modifier mixtures at 450 nm, from neat ACN to neat methanol (Fig. 4). Whatever, the mobile phase composition, the chromatograms obtained at 450 nm are made up of a double perturbation: negative and positive variations for the void volume band.

For the pure modifier (acetonitrile and methanol), the measurements carried out at 450 nm are identical

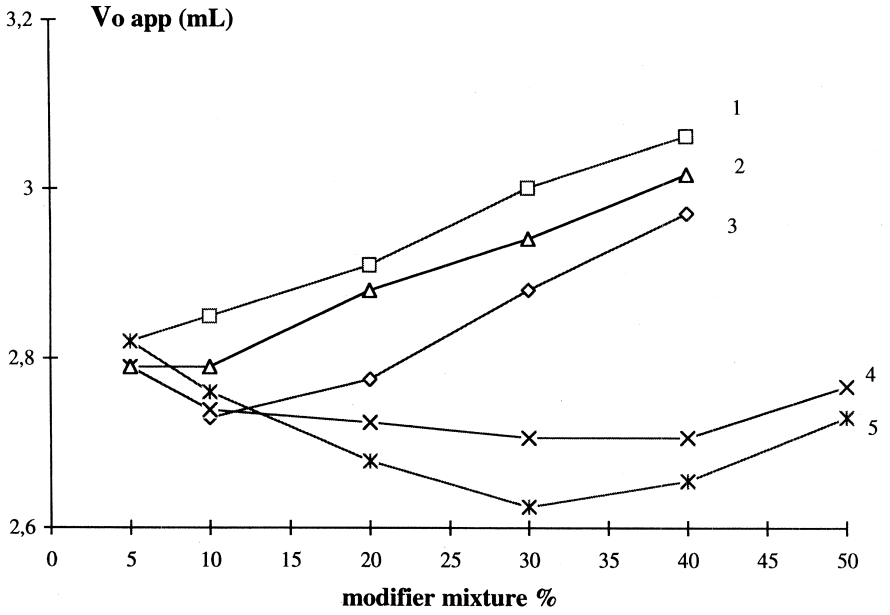

Fig. 4. $V_{0\ app}$ variations vs. ACN–MeOH modifier mixture percentage in CO_2 at 450 nm. **1**. Neat ACN. **2**. 80:20 (v/v). **3**. 50:50 (v/v). **4**. 20:80 (v/v). **5**. neat MeOH. Analytical conditions are described in Fig. 3.

to those obtained at 210 nm. The detection at 450 nm provides a reliable measurement procedure for the void volume. Moreover, the curves of V_0 variations plotted as a function of the modifier percentage decrease regularly from pure acetonitrile to pure methanol, that underlines the measurement accuracy of the void volume using this visible wavelength.

The selected methodology of V_0 measurement is: injection of neat ACN, detection at 450 nm and measurement of the void volume at the negative peak maximum. The peak is often negative with low modifier percentage, but becomes positive for a higher modifier amount, which requires an inversion of the polarity detection.

3.3. Explanation of the different V_0 variations

3.3.1. Variations with methanol and acetonitrile organic modifiers

Considering that the void volume is the total volume of eluent in the column [34], the void volume variations, can be explained by density variations of the mobile phase and by stationary phase volume variations, that are related to the physical or chemical properties of the modifiers. The measured dead volume, that corresponds to this total volume of eluent in the column, can be called the apparent dead volume ($V_{0\ app}$).

When the organic modifier is added to the carbon dioxide, the inlet pressure increases because of the greater viscosity of organic modifier. Consequently, internal pressure increases too, which leads to a mobile phase density increase. This phenomenon is true whatever the modifier nature and the modifier percentage added. However, the mobile phase density change does not modify the real void volume of the column, but only the molar volume of the eluent, i.e. the mobile phase volume that fills the void volume (the column porosity stays unchanged). Apparent-dead-volume variation could also be due to an adsorption of the mobile phase onto the stationary phase [18,19]. According to the modifier amount in the mobile phase, the range of this adsorption varies, which modifies the stationary phase volume, i.e. the void volume (the column porosity changes).

These two phenomena, density variation and variation of stationary phase volume can occur. With ACN, the increase in the apparent dead volume is mainly due to the mobile phase density increase (Fig. 4). With methanol modifier, the curve shows a minimum. First, when methanol percentage increases, the apparent dead volume decreases.

This underlines a methanol adsorption onto the stationary phase which is greater than the increase in the mobile phase density. This high methanol adsorption was reported elsewhere [19]. Secondly, with large methanol percentages, the apparent dead volume increases, because the increase on the mobile phase density becomes the greater phenomenon.

3.3.2. Relation between the apparent-dead volume and the chemical properties of the organic modifiers

Because the adsorption phenomenon of modifiers onto the octadecyl bonded stationary phase is due to interactions, i.e. the modifier chemical nature, a study of the apparent dead volume variation was done with other organic solvents as mobile phase modifiers. The different organic solvents used as modifiers can be classified into four groups from the different apparent-dead-volume variations (Fig. 5).

The classification obtained can be related to the distribution of these solvents in Hansen's triangle [35,36], which depends on the molecular interactions developed by these solvents (dispersion, hydrogen bond, dipole–dipole). Since the correlation between the apparent void volume variations and the molecular interactions occurs, the void volume measurement by acetonitrile injection seems to be a reliable method.

Acetonitrile, propionitrile and nitromethane are in this first group. The variation of apparent dead volume is identical for these three solvents, and mainly due to mobile phase density variations. This group is made up of solvents that interact essentially by dipole–dipole interactions, that explain the low affinity between these solvents and the octadecyl chains, and the low retention of the acetonitrile band (positive peak).

The second group contains alcohols: methanol and ethanol. The same curves are obtained for these alcohols, that underlines the great adsorption of the alcohols onto the stationary phase up to 20–25% of modifier in carbon dioxide.

The third group only contains heptane. The apparent dead volume decreases regularly when modifier percentage increases. The mobile phase adsorption onto the stationary phase is the predominant process, because this solvent has a good ability to establish dispersion interactions with the bonded octadecyl chains. It explains the high retention of heptane when this solvent is injected as dead-volume marker (Fig. 2).

This fourth group contains tetrahydrofuran, acetone and methylene chloride. The apparent dead volume slightly decreases as a function of the modifier percentage, which is indicative of an adsorption of modifiers onto the stationary phase compensated by the mobile phase density change. This low adsorption can be explained by the intermediary strength of dipole–dipole and dispersion interactions between those of the first group and those of the fourth group.

4. Conclusion

The main parameter operating on retention and separation of solutes in SubFC on ODS packed columns is the nature and the percentage of modifier. However, this involves some side effects: the variation of mobile phase density or adsorption of mobile phase components onto the stationary phase, which induce variations of the apparent dead volume. For the study of chromatographic behavior, these variations should be measured.

The simple method proposed for measuring apparent dead volume is the injection of ACN as a marker. The retention time of the first signal obtained with a UV/visible detector indicates the injection band. The detection and the measurement conditions were optimised to increase the accuracy of the results. This method is a dynamic one that allows taking into account every analytical condition change. Moreover, this method can be applied with high modifier percentages.

The results observed for dead volume variations according to modifier nature correlate quite well with a distribution based on physico-chemical properties.

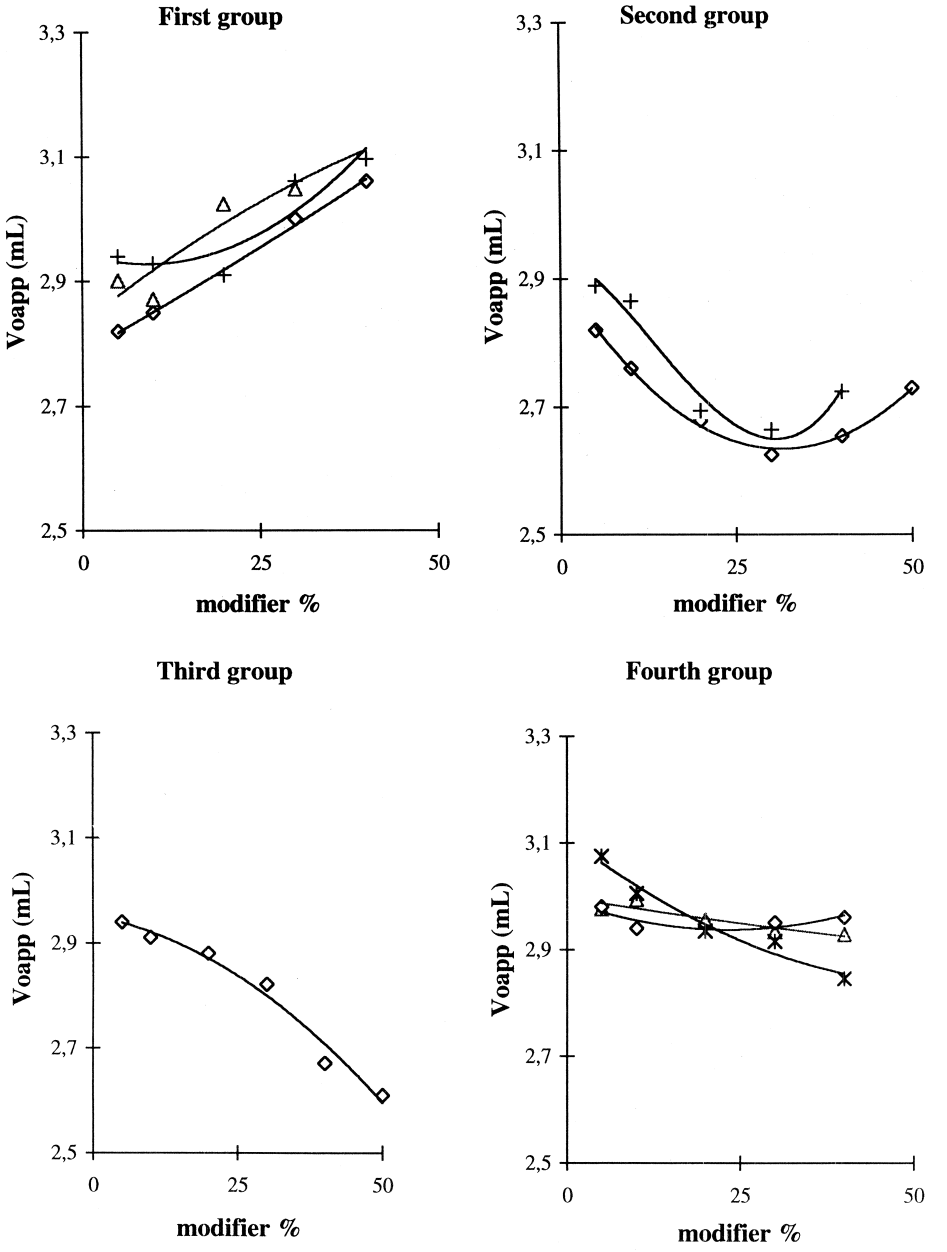

Fig. 5. $V_{0\ app}$ variations with nature and volumic percentage of modifier. *First group*: ◊ Acetonitrile; + Propionitrile; Δ Nitromethane. *Second group*:◊ Methanol; + Ethanol. *Third group*: ◊ Heptane. *Fourth group*: Δ Acetone; * Methylene chloride; ◊ THF. Analytical conditions are described in Fig. 3.

The void volume variations, observed for the four modifier groups, can be described by interactions between these organic modifiers and the stationary phase aliphatic chains.

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