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Journal of Chromatography A, 973 (2002) 177–186

JOURNAL OF CHROMATOGRAPHY A

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Ability of porous graphitic carbon to support electroosmotic flow in capillary electrochromatography

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Received 13 May 2002; received in revised form 26 July 2002; accepted 26 July 2002

Abstract

The existence of a cathodic EOF (electroosmotic flow) in the case of a porous graphitic carbon (PGC) partially packed column has been demonstrated. Then, the ability of PGC to afford electroosmosis has been brought to the fore with a fully PGC packed column. Experimental data have shown that PGC particles are negatively charged and their electrophoretic mobility has been evaluated. In order to investigate the conditions of existence of EOF different mobile phases have been tested. An EOF occurs when the conductivity of the PGC packed column is larger than the conductivity of an empty fused-silica capillary operating in the same conditions i.e. when the PGC participates in the electric conduction. Since the local electric fields in the two segments of the column are different, an evaluation of the electroosmotic mobility is not possible and the effect of the operational parameters such as the composition of the mobile phase (acetonitrile ratio and total ionic strength) has been studied in term of electroosmotic velocity v_{eo}.

Keywords: Electroosmotic flow; Electrochromatography; Porous graphitic carbon

1. Introduction

Capillary electrochromatography (CEC) is a liquid phase analytical separation technique that is carried out with capillary columns by the electroosmotically driven mobile phase [1]. The packing materials used in CEC are generally derived from liquid chromatography (LC) technology [2]. Standard C_{18} LC stationary phases were the first phases commonly used for CEC [3,4]. If the large majority of CEC separations are always realized using silica-based C_{18} bonded phases [5], the use of other phases such as C_8 and phenyl [6], cation-exchange phases [7–9], anion-exchange phases [10], mixed mode [11,12] and chiral phases [13,14] has been investigated.

Porous graphitic carbon (PGC) is a new column packing material recently available for LC [15]. Nevertheless, the potential of PGC as a stationary phase in CEC has never been explored to the best of our knowledge. PGC may present several advantages over other stationary phases in CEC and may extend the scope of CEC through the separation of geometrical isomers or of basic solutes or very polar solutes [16]. Its main advantage lies in its stability towards high pH electrolytes, allowing the separation of basic solutes in their neutral form by suppressing their ionization at high pH without any problem of

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)01122-6

stationary phase dissolution. Since the ability to support electroosmotic flow (EOF) is one of the most important properties of a column packing material for CEC, it is of utmost importance to investigate the conditions of generation of EOF and the ways of controlling and manipulating it.

2. Experimental

The stationary phase employed (PGC) was recuperated from a Hypercarb column, Nucleosil 1000-7 C_{18} stationary phase was purchased from Macherey-Nagel (Düren, Germany). Fused-silica capillaries (75 μm I.D.×375 μm O.D.) were obtained from Thermoquest Separation Products (Paris, France) and glass lined tube (30 cm×500 μm I.D.) from SGE (Paris, France). The frit fusing device was purchased from Innovatech (UK), the LC 10 AD*VP* liquid chromatography pump from Touzart et Matignon (France) and the ultrasonic bath from Bioblock (France). HPLC grade acetonitrile was obtained from Carlo Erba Reagents, acetone, carbon tetrachloride (CCl_4), citrate, and tris (hydroxymethyl)-methylamine TRIS from Aldrich Chemical Company (Gillingham, UK). The mobile phases were degassed by ultrasonication prior to use and solutions of analytes were prepared in the mobile phase.

3. Instrumentation

CEC experiments were performed on a $HP^{3D}CE$ (Hewlett-Packard, Waldbronn, Germany) equipped with a diode array detector operated at 245 nm. All experiments were carried out at 25 °C. A pressure of 10 bars provided by pressurized nitrogen was applied at both ends of the capillary to prevent bubble formation. Samples were injected hydrodynamically by application of a pressure of 5 bars for 12 s.

4. Procedures

4.1. Column preparation

Prior to the packing procedure with PGC, the outlet frit has to be created from a silica based stationary phase at a distance of ca. 10 cm of the capillary extremity. Therefore, a retaining frit was made by packing the capillary with 1000-7 C_{18} followed by sintering this phase with the frit fusing device and excess of C_{18} stationary phase was removed from both sides of the frit as previously described [17]. The PGC was slurried in CCl_4 at a concentration of 20–30 mg ml^{-1} and the suspension placed in an ultrasonic bath for 5 min. The slurry was then poured into the glass lined tube connected to the capillary and to the LC pump. Acetonitrile was used as pumping solvent. During the packing procedure, the slurry reservoir was placed in the ultrasonic bath to prevent settling out of the stationary phase. The initial flow-rate was set at 60 μl min^{-1} until the pressure reached 400 bars. The packing pressure was further maintained at 400 bars until the desired length of capillary had been reached, the system was then allowed to depressurize. Then, the capillary was refilled with the 1000-7 C_{18} stationary phase in order to create the inlet frit.

A detection window was made at 2 mm from the outlet frit by burning the polyimide coating using the same hot filament device. The column was then flushed with the mobile phase at 200 bars with the LC pump.

5. Results and discussion

5.1. Aptitude of PGC to support EOF

First of all, in order to determine the aptitude of the PGC packing material to afford an EOF, the existence and magnitude of the EOF was evaluated in the case of an entirely PGC packed column in order to eliminate the contribution of the open segment to the EOF occurring in a partially packed column. Therefore the whole capillary was packed with PGC, the packing material being retained by two silica frits as described in the experimental part.

Due to the lack of a detection cell, it is obvious that the determination of the magnitude of EOF in such a column cannot be realized by injection, migration and detection of an EOF marker. The EOF should be evaluated by estimation of the mass of mobile phase transferred during a given time [18,19]. The validity of this method was verified by compar-

ing the EOF values obtained with an EOF marker and by mass transfer in the case of an empty fused-silica capillary and a partially PGC packed column and the results compared to those obtained in the case of a C_{18} (7 μm–1000 Å) silica based packed column.

The values of electroosmotic velocities v_{eo} measured in the same conditions of mobile phases, capillary geometry and voltage (10 kV applied at the anodic extremity) are summarized in Table 1. First, the comparison between values of electroosmotic velocities estimated by mass transfer or by UV detection of an EOF marker (in the case of an empty fused-silica capillary, a partially C_{18} or PGC packed capillary) indicates that the mass transfer method gives a reasonable estimation of the value of the electroosmotic flow although the values obtained with this method seem to be slightly overestimated. The differences between the values obtained with the two methods are probably due to the very low mass differences measured by mass transfer (from a few mg to 30 mg) and to the calculation method including the estimation of the porosity of the column ($\varepsilon = 0.8$) and the of the density of the mobile phase (0.8). Besides, these results indicate the existence of a substantial EOF, directed towards the cathodic extremity, in a fully PGC packed column. The electroosmotic velocity in the case of a PGC fully packed column (mean value 0.144 cm s^{-1}, for an applied electric field of ca. 288 V cm^{-1}) is three times higher than the velocity observed in the case of a fully C_{18} packed column indicating that, in these experimental conditions, the PGC material affords an electroosmotic flow much more important than the C_{18} material. As expected, the electroosmotic flows in a fully C_{18} packed column and in a partially C_{18} packed column are quite identical (local electric fields and electroosmotic mobilities in the empty and packed sections of the capillary are of the same order of magnitude in the experimental conditions of mobile phase), but no prediction could be done for PGC columns owing to the absence of information in the literature about the behavior of this material under voltage.

Moreover, experimental values of the currents determined in each experimental conditions (Table 1) show that the currents across the PGC packed columns (fully or partially packed column) are higher than those observed across an empty fused-silica capillary having the same dimensions or across a C_{18} packed column (fully or partially packed column) and operating in the same experimental conditions. These observations suggest that the electric conduction, in the case of a column containing PGC particles, cannot not be exclusively attributed to the electrolyte but to PGC particles too, i.e. the

Table 1
v_{eo} estimated by mass transfer and by detection of an EOF marker

	v_{eo} estimated by mass transfer (cm s^{-1})	v_{eo} estimated by detection of an EOF marker	I (μA)
Fused silica capillary	0.239* ($n=3$, RSD=9%)	0.215 ($n=3$, RSD=1.7%)	1 μA
Partially PGC packed column	0.120* ($n=3$, RSD=11%)	0.101 ($n=3$, RSD=3.9%)	4.5 μA
Fully PGC packed column	0.134** 0.154* ($n=2$, RSD=10%)	–	7 μ A
Fully C_{18} packed column	0.05* ($n=3$, RSD=18%)	–	0.9 μA
Partially C_{18} packed column	0.048 ($n=3$, RSD=21%)	0.046 ($n=3$, RSD=2.3%)	0.7 μA

Mobile phase: 90/10 ACN/Tris 10 mmol l^{-1} pH 8. V=10 kV; porosity of PGC packed column=80%; porosity of C_{18} packed column=80%; density of the mobile phase=0.8; transfer during 60 min: *; transfer during 95 min: **; fused-silica capillary: l=24 cm; L=32.5 cm; partially PGC packed column: l=34.7 cm; L=43.2 cm; fully PGC packed column: $l = L = 34.7$ cm (the empty section of the partially packed column was cut); fully C_{18} packed column=33.8 cm (the empty section of the partially packed column was cut); partially C_{18} packed column l=33.8 cm; L=42.3 cm.

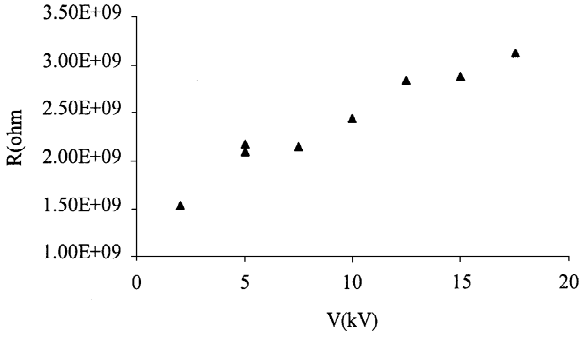

Fig. 1. Resistance vs. voltage in a fully PGC packed column. Column: $l = L = 33.5$ cm. Mobile phase: ACN/Tris 10 mmol l^{-1} pH 8 (90/10).

electrical conduction is achieved by both the ions of the electrolyte (ionic conduction) and the electrons of the PGC material (electronic conduction). This is in accord with the well-known fact that graphite is an electrical conductor [16]. The C_{18} silica frits retaining the PGC material in the PGC columns cannot be responsible for such an increase in current since it has been verified that the presence of such a C_{18} frit in an empty fused-silica capillary frit systematically increases its resistance. Moreover, as illustrated in Fig. 1, the resistance of an entirely PGC packed column increases with the voltage. Although such a behavior could be first attributed to resistive heating (in a material in which electronic conduction occurs, the resistivity increases with temperature i.e. with joule heating) it appears as improbable owing to the small value of the power dissipated by the joule effect in the experimental conditions used throughout this study ($P < 0.1$ Watt).

6. Surface charge of PGC

The existence of a cathodic EOF generated by PGC particles suggests the presence of negative surface charges on PGC particles. In order to verify this assumption, two experiments have been performed.

In the first experiment, the anodic inlet frit of a PGC column was cut and a positive electric field was applied across the column operating with a 95/5 (ACN/Tris 20 mmol l^{-1} pH 8) mobile phase. The PGC particles migrated to the anodic electrode against the cathodic EOF, indicating that the PGC particles are negatively charged.

Table 2
Electroosmotic mobility and electrophoretic mobilities of PGC particles

Voltage (kV)	μ_{eo} ($cm^2\ s^{-1}\ V^{-1}$)	μ_{ep} ($cm^2\ s^{-1}\ V^{-1}$) ($n=3$)
−5		$9.12\ 10^{-4}$ (RSD = 1.3%)
−10	$-6.34\ 10^{-4}$	$9.21\ 10^{-4}$ (RSD = 1.8%)
−20	($n=3$, RSD = 1.6%)	$9.24\ 10^{-4}$ (RSD = 1.9%)
−25		$8.96\ 10^{-4}$ (RSD = 2.1%)
−30		$9.24\ 10^{-4}$ (RSD = 1.9%)

Mobile phase: 95/5 ACN/Tris 20 mmol l^{-1} pH 8; fused-silica capillary: $l = 25$ cm; $L = 32.5$ cm; $T = 25$ °C; injection 50 mbar, 2s.

The second experiment consisted in the determination of the electrophoretic mobility of PGC particles in the same conditions of mobile phase. Firstly, the electroosmotic mobility was evaluated by the injection of acetone as an electroosmotic flow marker in an empty fused-silica capillary. Secondly, a suspension of PGC particles prepared in the mobile phase was injected in the same capillary and the detection of the particles was realized at 200 nm. When operating in the positive mode (anodic injection), the particles did not reach the detector. The detection of the PGC particles at the anodic extremity was only possible when a negative voltage was applied across the column (cathodic injection). The values of electroosmotic mobility μ_{eo} and electrophoretic mobilities μ_{ep} of PGC particles determined at different voltages are summarized in Table 2. These values confirm the negatively charged surface of PGC particles and indicate that the surface charge of PGC does not depend on the applied voltage since the μ_{ep} of the particles are constant between 5 and 30 kV (mean value 9.13×10^{-4} $cm^2\ s^{-1}\ V^{-1}$, RSD = 1.3%). Nevertheless, it seems difficult to affirm if the surface charges are permanent or due to the application of the electric field across the column.

7. EOF in PGC partially packed columns

Further experiments were realized on partially packed columns since such columns are generally used in CEC to allow UV detection in the open

segment of the capillary and since it is more convenient to measure EOF by the detection of an electroosmotic flow marker (one EOF measurement by mass transfer requires at least 1 h experiment owing to the very small volumes of liquid transferred by EOF). However, the use of partially packed beds makes the interpretation of the data more complex. In fact, such a partially packed column consists of a packed segment (PGC particles retained by two C_{18} frits) and an open segment of lengths L_{packed} and L_{open} respectively. It means that the column is axially inhomogeneous in term of local resistivity and of local electric fields. Owing to the small length of the silica frits (about 1.5 mm in length for each frit) compared to the length of the packed bed (at least 23 cm) only two different zones were considered in the partially packed column, the ''open'' and the ''packed'' one, the packed one being constituted of the silica frits and the PGC stationary phase. When an electric field E is applied, the ratio of local electric fields E_{packed} and E_{open} depends on the resistivities ratio (ρ_{packed} and ρ_{open}). The evaluation of E_{packed} and E_{open} implies the determination of the local voltages V_{packed} and V_{open} when I is the current flowing through the PGC partially packed column when a potential drop V is applied across this column of a global resistance R.

In order to determine V_{open}, the resistance of the open segment R_{open} has to be evaluated. R_{open} can be calculated once the resistance R' of an empty fused-silica capillary of length L', filled with the same electrolyte and having the same section, is known. R_{open} can be evaluated using the following expression:

$$R_{open} = R'L_{open}/L \quad (1)$$

$$V_{open} = IR_{open} \quad (2)$$

Packed and open segments of the CEC column being connected in series, R_{packed} can be calculated as follows:

$$R_{packed} = R - R_{open} \quad (3)$$

$$V_{packed} = IR_{packed} \quad (4)$$

Once V_{packed} and V_{open} are calculated, E_{packed} and E_{open} can be evaluated as follows:

$$E_{packed} = V_{packed}/L_{packed} \quad (5)$$

$$E_{open} = V_{open}/L_{open} \quad (6)$$

The higher the difference between the currents measured in the PGC partially packed column and in an empty silica capillary, the higher the conductivity of the PGC segment and the lower the local electric field E_{packed} in the packed section.

In a partially packed column an average electroosmotic flow, depending on the relative contributions of the two different segments, will be established across the whole column in order to satisfy the mass conservation law. This electroosmotic flow is a function not only of the electroosmotic mobility of each segment ($\mu_{eo\ open}$ and $\mu_{eo\ packed}$) but also of the local electric fields (E_{open} and E_{packed}). If the local electric field E_{open} in the open segment is very high (owing to its high resistivity), one may suppose that the empty segment of fused-silica plays the role of an EOF accelerator segment as described by El Rassi and al. [20].

Therefore, according to the inhomogeneity of the electric field in a partially packed column, the calculation of the electroosmotic mobility is not possible and the magnitude of EOF is evaluated in term of electroosmotic velocity v_{eo}.

7.1. Efficiency of PGC partially packed columns

In order to evaluate the chromatographic performances of the home-made PGC partially packed columns, their efficiencies were calculated for an unretained solute (acetone) in presence of an hydro-organic mobile phase (95/5 acetonitrile/Tris 20 mmol l^{-1} pH 8) at different mobile phase velocities. The average optimal efficiency was around 90 000 plates/m (5 columns tested, RSD = 15%) at the optimal linear velocity of ca. 0.1 cm s^{-1} (H = 11.2 μm). The chromatogram illustrated in Fig. 2 represents the separation of two phenylurca (fenuron and isoproturon) at a linear velocity of ca. 0.12 cm s^{-1}: the efficiencies (N = 80 000 plates/m for both compounds) calculated for these two retained solutes ($k = 0.74$ and $k = 1$ respectively) show that good efficiencies are not only attainable for unretained solutes but also for retained ones.

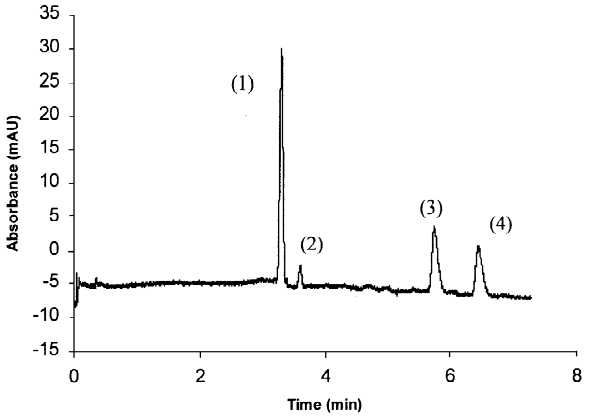

Fig. 2. Electrochromatogram of acetone (injected as electroosmotic flow marker), fenuron and isoproturon. PGC partially packed column: $l = 23.4$ cm, $L = 31.9$ cm. Mobile phase: ACN/Tris 20 mmol l^{-1} pH 8 (95/5), $T = 25$ °C, $V = 10$ kV, $I = 3.1$ μA, injection 5 kV during 2s. N(acetone) = 19 000, N(fenuron) = 18 700 plates, N(isoproturon) = 18 300 plates. (1) acetone, (2) impurity, (3) fenuron, (4) isoproturon.

7.2. Conditions of existence of EOF in partially packed columns

In order to investigate the conditions of existence of EOF with PGC partially packed columns a great variety of mobile phases have been tested. All these experiments have revealed the existence of a cathodic EOF, measured after the injection of acetone as EOF marker and application of a positive electric field. Moreover, experimental data illustrated Fig. 3 (at least 3 replicates for each mobile phase), have shown that the existence of an EOF in a PGC packed column seems to be related to its conductivity: an EOF, the magnitude of which depends on the mobile phase composition, is observed in the PGC packed column when the current across the partially PGC packed column is greater than the current observed across an empty fused-silica capillary having the same dimensions and operating in the same conditions, i.e. when PGC contributes to the

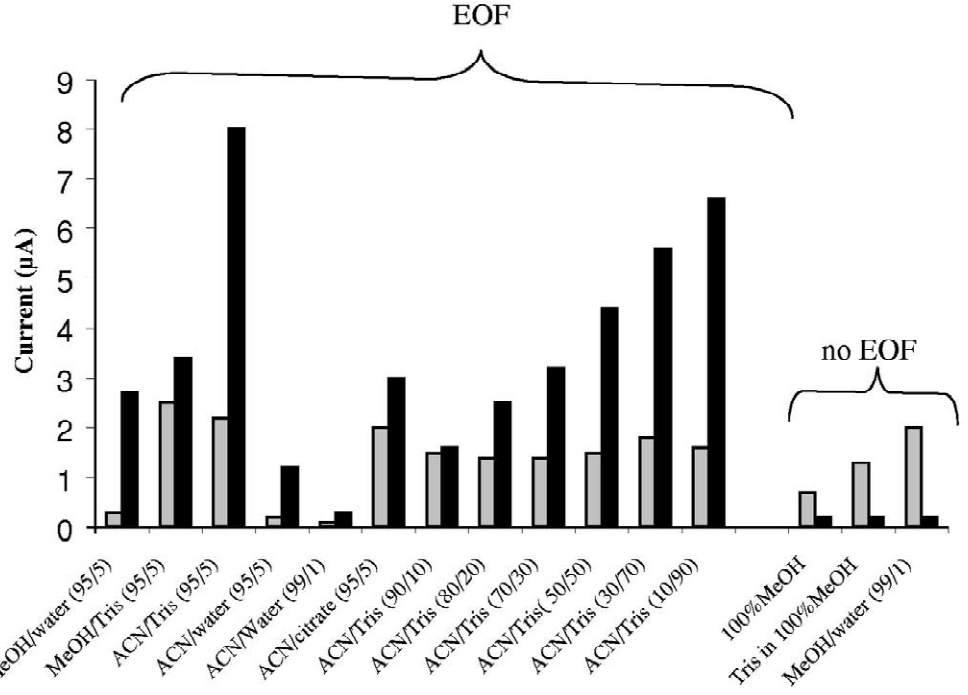

Fig. 3. Comparison of the current values I in an empty fused-silica capillary and in a partially PGC packed column with different mobile phases. Buffers: Tris pH 8, citrate pH 3.5. Empty fused-silica capillary: $l = 23.5$ cm; $L = 32$ cm, partially PGC packed column: $l = 23.5$ cm; $L = 32$ cm. (▒) I (empty), (■) I (PGC).

electric conduction. The absence of electroosmotic flow with mobile phases containing 99 or 100% MeOH is not due to the quality of the column (porosity of the frits ...) since a substantial EOF was obtained on the same column with hydroorganic acetonitrile mobile phases. Moreover, bubble formation cannot account for a breakdown of the electroosmotic flow and for the abnormally low value of the current since the current never established in the capillary even at the beginning of the experiment and at a low value of electric field and since no bubbles were detected in the UV trace when the capillary was immediately flushed at a pressure of 10 bars during 30 min (only 20 min are necessary to replace the whole content of the mobile phase of the capillary column). No valuable explanation can be proposed to account for this particular behavior.

7.3. Influence of the voltage on the current

The effect of the applied voltage on the current was studied in the case of 3 columns having the same dimensions and with a 95/5 ACN/Tris (20 mmol l^{-1} pH 8) mobile phase. As illustrated in Fig. 4 the electric current values differ from one column to another while the same voltage is applied. It means that the total resistance and particularly the resistance of the packed segment varies from one column to another: this difference may be due either to the arrangement of the stationary phase particles (i.e. to the quality of the packing bed) or to the silica frits, the porosity of which may vary from one column to another and alter the global resistance of the packed segment. Besides, the rolloff at the high voltage end of the curve is probably due to the alteration of the resistance of the PGC packed segment with the voltage as mentioned before.

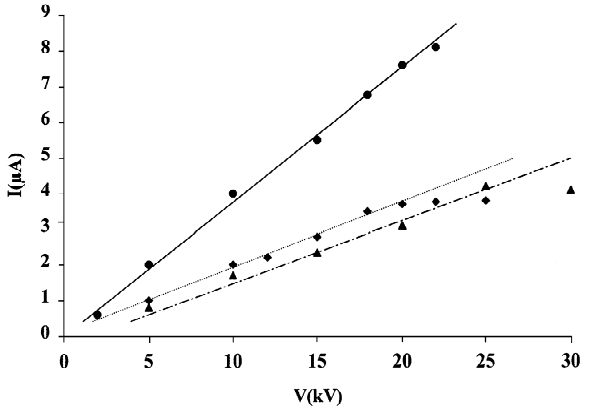

Fig. 4. Current vs. voltage in partially packed columns. Column 1: $l=24.2$ cm; $L=33$ cm; Column 2: $l=23.2$ cm; $L=31.9$ cm; Column 3: $l=24$ cm; $L=32.7$ cm. Mobile phase: ACN/Tris 20 mmol l^{-1} pH 8 (95/5). (♦) column 1, (●) column 2, (▲) column 3.

7.4. Influence of the voltage on the electroosmotic velocity

The effect of the voltage on the electroosmotic velocity v_{eo} was studied in the case of the same three columns and in the same conditions of mobile phase. The electroosmotic velocity (at least 3 replicates, with relative standard deviations ranging from 1.5 to 4.5%) was plotted against the total electric field applied between the two extremities of the column and against the electric field in the open segment (E_{open}) as represented in Fig. 5. If the velocities (versus the total electric field) are roughly equivalent for columns 1 and 2, they are significantly different for column 3: for a total electric field of ca. 600 V cm^{-1}, the electroosmotic velocities are respectively 0.245 cm s^{-1} and 0.258 cm s^{-1} for columns 1 and 2 but it falls to 0.172 cm s^{-1} for column 3.

These results are not surprising: first, the difference in resistance from one column to another leads to a variation in local electric fields E_{packed} and E_{open} and consequently to a modification of the relative contributions of the two segments to the total EOF and secondly, the variation of the porosity of the silica frits may also account for such small variations. Besides, as shown in the expanded region of Fig. 5 the departure from the linear model observed especially for column 1 and to a lesser extent for column 3 at high voltages is probably due to the alteration of the resistance of the PGC packed segment with the voltage as previously described. The rolloff at the high voltage tends to show that joule heating at high voltages is not responsible for the increase in the resistivity mentioned before since it should have led to an increase in electroosmotic velocity consecutive with the decrease in the mobile phase viscosity with joule heating.

Furthermore, in order to verify if the electroosmotic flow in a partially packed column is gov-

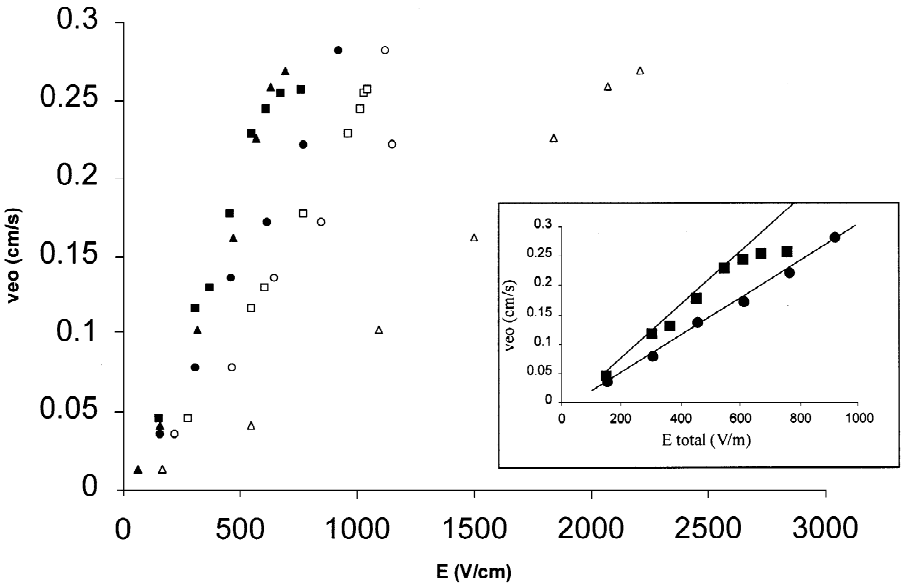

Fig. 5. Electroosmotic velocity vs. the global electric field or versus the electric field in the open segment E_{open}. Column 1: (l=24.2 cm; L=33 cm), (■) E_{total}, (□) E_{open}; Column 2: (l=23.2 cm; L=31.9 cm), (▲) E_{total}, (△) E_{open}; Column 3: (l=24 cm; L=32.7 cm), (●) E_{total}, (○) E_{open}. Mobile phase: ACN/Tris 20 mmol l^{-1} pH 8 (95/5).

erned by the open section that ''acts as a pump'' (owing to the high local electric field in the open segment of high resistivity), the electroosmotic velocity was also plotted versus the local electric field in the empty segment E_{open} as shown in Fig. 5. Although v_{eo} and E_{open} seem to be well correlated, the EOF cannot be exclusively attributed to the open segment since different electroosmotic velocities are obtained for the same E_{open} value.

7.5. Influence of proportion of ACN on the electroosmotic velocity

The effect of the proportion of ACN on the electroosmotic velocity v_{eo} was studied at a constant ionic strength (1 mmol l^{-1} Tris pH 8) at a voltage of 15 kV. As shown in Fig. 6, an increase of 100% of the electroosmotic velocity is observed when the proportion of ACN is decreased from 95 to 10%. This behavior is quite different from that observed in a column packed with a non conductive stationary phase, as an increase of the EOF is generally observed when increasing the ACN ratio from 0 to 80% [21–27].

This behavior can be related to the change in the relative local electric fields in the two segments with the acetonitrile ratio. In fact, when plotting the electroosmotic mobility $\mu_{eo(open)}$ measured with these mobile phases in an empty fused-silica capillary and the local electric field in the open segment E_{open} (evaluated as described before) versus the ACN composition, the increase of v_{eo} observed in the partially packed PGC columns when reducing the ACN composition seems to be essentially due to the

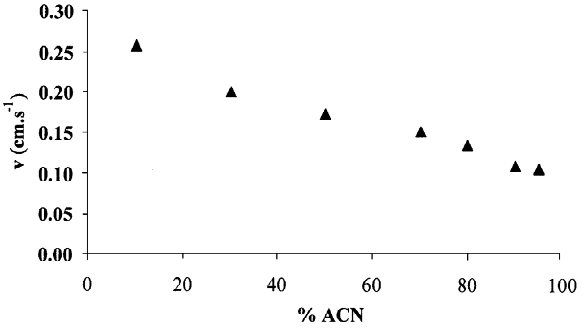

Fig. 6. Electroosmotic velocity v_{eo} in a partially packed column vs. ACN ratio: l=23 cm; L=31.7 cm; V=15 kV. Mobile phase: ACN/Tris 20 mM pH 8/water (x/5/100 − 5 − x).

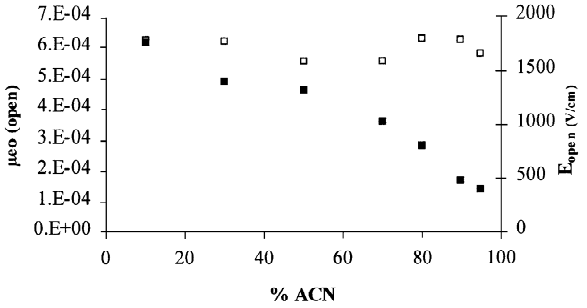

Fig. 7. Electroosmotic mobility in the open segment $\mu_{eo\ (open)}$ and electric field in the open segment E_{open} vs. ACN ratio: $l=23$ cm; $L=31.7$ cm; $V=15$ kV. Mobile phase: ACN/Tris 20 mM pH 8/water ($x/5/100-5-x$. (■) $E_{(open)}$, (□) $\mu_{eo\ (open)}$.

increase of the contribution of the open segment to the total EOF subsequent to the increase of the electric field in the open segment E_{open}, whereas the electroosmotic mobility $\mu_{eo(open)}$ is less affected as illustrated in Fig. 7.

7.6. Influence of the electrolyte concentration on the electroosmotic velocity

The incidence of the ionic strength on the electroosmotic velocity was studied with a 90% ACN mobile phase at a voltage of 20 kV when varying the total electrolyte concentration between 0 and 4 mmol L^{-1}. The concentration of the electrolyte seemed to have little effect on the electroosmotic velocity v_{eo}.

8. Conclusion

To the best of our knowledge it is the first time that the use of PGC in capillary electrochromatography is related. In this paper, we demonstrate the ability of PGC particles to afford EOF, although this fact can be surprising due to the high hydrophobicity of this chromatographic material. The existence of a cathodic EOF suggests that PGC is negatively charged, and this hypothesis has been verified by measuring the electrophoretic mobility of PGC particles. This observation is not contradictory with the fact that PGC particles possess specific retention properties towards anions, since these interactions are not described as electrostatic ones but result probably from electronic orbitals overlap [16,28].

However the situation in a partially packed column is quite complex, since we have demonstrated that the participation of PGC in the electrical conduction leads to an inhomogeneity in the electric field that impairs the calculation of a global electroosmotic mobility. Actually, the contribution of the packed section to the total EOF in a partially packed column seems to be difficult to estimate since the local electric field in the open segment of the column is much greater than the local electric field in the packed segment.

In order to overcome this difficulty and to determine if porous graphitic carbon will be a useful material for CEC, it should be preferable to work with fully packed columns and therefore to hyphenate capillary electrochromatography to mass spectrometry.

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