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Study of electroosmotic flow in packed capillary columns

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Abstract

The aim of the work was to find the relationship between the structure of the stationary phase and the velocity of the electroosmotic flow (EOF) that it can generate. The attention was paid to the dependence of the electroosmotic mobility (μ_{EOF}) on such parameters as: (i) coverage density of a series of specially synthesized C_{18} stationary phases with/without end-capping, with monomeric/polymeric architecture; (ii) the length of the alkyl chain in the alkylamide (AP) bonded phase (the phases studied were AP with: C_1, C_5, C_6, C_7, C_8, C_{12} and C_{18} alkyl chains) and the effect of the presence of amide and residual amine groups; (iii) the effect of the mobile phase composition on the EOF; (iv) the effect of pH on the EOF. The obtained results have shown that there is no direct relationship between silanol activity (Galushko test) and electroosmotic mobility for C_{18} phases. The deterioration of the EOF has been observed for AP phases at high pH values. This effect has been attributed to the presence of *hydrolytic pillow*, which is connected with the sorption of water from hydro-organic mobile phases.

Keywords: Electroosmotic flow; Packed capillary columns; Electrochromatography; Stationary phases, electrochromatography; Electroosmotic mobility; Mobile phase composition; pH effects

1. Introduction

The evolution of liquid chromatography, which could be observed during last decades displays two tendencies. Firstly, new stationary phases are still being developed, which results in obtaining highly specific materials dedicated to special applications. Classical particulates, silica-based as well as monolithic materials are synthesized. Secondly, chromatographic systems are miniaturized, which results in the construction of capillary columns and chip devices. Moreover, great advances in electromigration techniques, particularly in zone electrophoresis and its various modes, provided new possibilities in separation techniques [1–3].

Capillary electrochromatography (CEC) is a separation technique considered as a hybrid of liquid chromatography and capillary electrophoresis. In CEC, liquid chromatographic stationary phases are used together with the electroosmotic flow (EOF) generated in capillary columns. The flat profile of the EOF makes the electrochromatographic sepatrations more efficient compared to pressure-driven systems.

The electroosmotic flow is a phenomenon that makes it possible to perform electrochromatographic separation, provided that the linear velocity of the mobile phase that can be generated in a packed capillary is relatively high. The EOF in a bare fused silica capillary is connected with the presence of the electric double layer of cations (a fixed layer and a diffuse layer) on the capillary wall. Consequently, silica particles—also possessing silanol groups—exhibit the same effect. Hence, the role of the stationary phase in CEC is not limited to the separation itself (the phenomena and interactions that lead to separation) but it should also ensure the mobile phase flow fast enough to perform the separation process within a reliable time.

The linear velocity of the mobile phase is described by the following equation:

$$u_{EOF} = \frac{\varepsilon_0 \varepsilon_L \zeta E}{\eta} \quad (1)$$

where ε_0 is the permittivity of a vacuum, ε_L the permittivity of a liquid mobile phase, ζ the zeta potential, E the electric field strength and η a mobile phase viscosity. For a comparison of different systems or systems employed under various conditions it is more convenient to use the electroosmotic mobility (μ_{EOF}) that can be calculated in the following way:

$$\mu_{EOF} = \frac{u_{EOF}}{E} = \frac{L_{tot} L_{eff}}{t_0 V} \quad (2)$$

where L_{tot} and L_{eff} are total and effective (from the inlet to the detection window) lengths of the capillary, t_0 is the

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retention time of a non-retained compound, and V is the voltage applied.

Neglecting the experimental parameter, i.e. the electric field (E), the linear velocity u depends on the zeta potential, which in turn is connected with the concentration of surface polar groups (e.g. silanol), degree of their ionization (pH-dependent or not) or the concentration of the buffer.

In theory, the wall of a fused silica capillary as well as the stationary phase should generate the EOF. However, Smith and Evans [4] reported that in such a system (a capillary packed with a stationary phase) the electroosmotic mobility depended on the properties of the stationary phase, despite the fact that the EOF was ca. threefold faster (at pH 9.0) in an open capillary. Moreover, the authors did not indicate any differences in the electroosmotic mobility for columns prepared with non-modified and modified (polyvinyl alcohol coating to eliminate the EOF) fused silica capillaries.

The studies by Zimina et al. [5] show that the comparison of different stationary phases (provided by different producers) does not lead to any general conclusion regarding the influence of the stationary phase on the EOF (except an increase in the EOF with specific surface area of the silica material).

This paper presents the results of a study of the electroosmotic flow generated on two series of specially synthesized stationary phases characterized by controlled surface properties. In the first group we studied C_{18} phases and the following parameters were taken into account: coverage density, end capping and silane functionality. The second series was a specially synthesized series of alkylamide (AP) phases with alkyl chains of different lengths.

2. Experimental

2.1. Materials and chemicals

Phosphoric acid (85%), acetic acid (95.5%), boric acid, sodium hydroxide, hydrochloric acid, methanol and thiourea were of analytical grade, acetonitrile (ACN) was of HPLC grade and these chemicals were purchased from Polskie Odczynniki Chemiczne (POCh, Gliwice, Poland). Tris(hydroxymethyl)aminomethane (Tris) was purchased from Merck (Darmstadt, Germany). Deionized water was obtained in our laboratory using the Milli-Q (Millipore, Bedford, MA, USA) equipment.

Table 1
Characteristics of silica support Kromasil 100, batch AT 0191 (Akzo-Nobel)

Parameter	Symbol	Unit	Value
Particle shape		–	Spherical
Particle size	d_p	μm	5
Specific surface area	S_{BET}	m^2/g	295
Mean pore diameter	D	Å	113
Pore volume	V_p	cm^3/g	0.92
Concentration of hydroxyl groups	α_{OH}	$\mu mol/m^2$	7.1
Concentration of metal impurities	c_M	ppm	<20

Buffers were prepared by dissolving in water the appropriate amounts of phosphoric acid, acetic acid, Tris or boric and adjusting pH with 1.0 M NaOH or 1.0 M HCl. The buffers covered a wide range of pH values: phosphate buffers of pH 2.5, 6.5, 7.5; acetate buffers of pH 4.0 and 5.0; Tris at pH 8.5 and borate at pH 9.5. For all experiments the buffer concentration was 5 mM. To prepare a mobile phase each buffer was mixed with acetonitrile at the desired volume ratio. Then the mobile phase was degassed using sonication under vacuum.

The synthesis of a series of C_{18} stationary phases was described elsewhere [6]. The characteristics of the silica support (Kromasil 100, Akzo-Nobel, Bohus, Sweden) are shown in Table 1, while the description of synthesized stationary phases is presented in Table 2. The synthesis and properties of alkylamide phases are described in details in papers [7,8].

2.2. Columns

The 100 μm i.d. fused silica capillaries (Polymicro) were purchased from Composite Metal Services (Worcester, UK). The capillaries were packed with the stationary phases using a home-made set-up consisting of a DSF-122 (Haskel, Burbank, CA, USA) pump, a stand for slurry reservoir (50 mm × 2 mm) and a capillary. The integral part of the stand is a device for sintering the frits. The capillaries were packed

Table 2
Characteristics of C_{18} stationary phases of controlled coverage density

Packing abbreviation	Phase	C (%)	H (%)	α_{RP} ($\mu mol/m^2$)	Surface coverage density (%)
MLCD	Monomer	10.66	2.48	1.75	23.3
MLCD-EC	Monomer	12.68	2.86	2.13	28.5
MHCD	Monomer	17.10	3.63	3.10	41.5
MHCD-EC	Monomer	17.45	3.85	3.17	42.4
DLCD	Polymer	16.02	3.36	3.27	43.8
DLCD-EC	Polymer	16.84	3.60	3.40	45.5
DHCD	Polymer	17.35	3.74	3.64	48.7
DHCD-EC	Polymer	17.38	3.75	3.71	49.6

CD: coverage density, M: monomeric, D: polymeric, L: low coverage density, H: high coverage density, EC: end capping, C (%) and H (%): percentages of carbon and hydrogen content, respectively.

using methanol (50 MPa); then, during flushing with water (50 MPa) the frits were sintered. Finally, the detection window was created by scraping the polyimide coating with the sharp edge. All the columns had the same dimensions: $L_{tot} = 33.5$ cm, $L_{eff} = 25$ cm.

2.3. CEC

All the experiments were performed using the HP^{3D}CE system (Agilent Technologies, Waldbronn, Germany) dedicated to CEC separations, equipped with a diode array detection (DAD) system and ChemStation software for control and data collection. If not stated otherwise the following experimental conditions were applied: $V = +20$ or -20 kV, injection $+5$ or -5 kV for 3 s, temperature 25 °C; UV spectrophotometric detection was performed at $\lambda = 200$ or 254 nm.

3. Results and discussion

3.1. Effect of pH on electroosmotic mobility—C_{18} materials

In order to obtain stable and comparable electroosmotic flow, the capillaries were fully packed with C_{18} stationary phases (see Experimental section). Moreover, there is an additional advantage of such a solution—the problem of bubble formation is eliminated. In such columns parts of different electroosmotic mobilities (open and packed) do not exist, however in some cases the problem of drying of the outlet part of the bed occurs.

The influence of pH on the EOF generated by C_{18} stationary phases was determined using the mobile phases containing acetonitrile—buffer (70:30, v/v). For each column, the experiments began with the buffer of the lowest pH, that is 2.5, then pH gradually increased. In this way the effect of hysteresis [9] did not influence the results. Before starting the experiments, each column was equilibrated for 1 h under EOF conditions using appropriate mobile phase. This amount of time was needed to stabilize EOF after each change of the buffer (mobile phase). The procedure was the same for all columns, to provide reliable results.

As expected, the electroosmotic mobilities increase with the pH for each of the stationary phases (Fig. 1). However, there is no clear tendency of change in μ_{EOF} accompanying the change in the stationary phase structure, even at high pH, when all silanols are ionized. Surprisingly, quite high values of μ_{EOF} were determined at low pH. Some authors [10] attribute such effects to the impurities of the silica support. Silica can be contaminated not only with metal ions, but also with sulfate or carbonate ions. All of these individuals can contribute to the creation of surface charge and, in consequence, affect the EOF. A very interesting observation is that only at low pH the differences in electroosmotic mobilities between not end-capped materials and end-capped analogues can be explained by their different coverage densities and the application of end-capping to reduce the amount of residual silanols. For example the MLCD phase generated EOF much faster than the MLCD-EC phase. At high pH, when all silanols are ionized these differences are not so easy to explain.

3.2. Silanol activity versus electroosmotic mobility

The silanol activity tests usually provide the information on the effect of residual silanol groups on the polar compounds. All the known tests are dedicated to HPLC conditions where non-buffered mobile phases are used. We

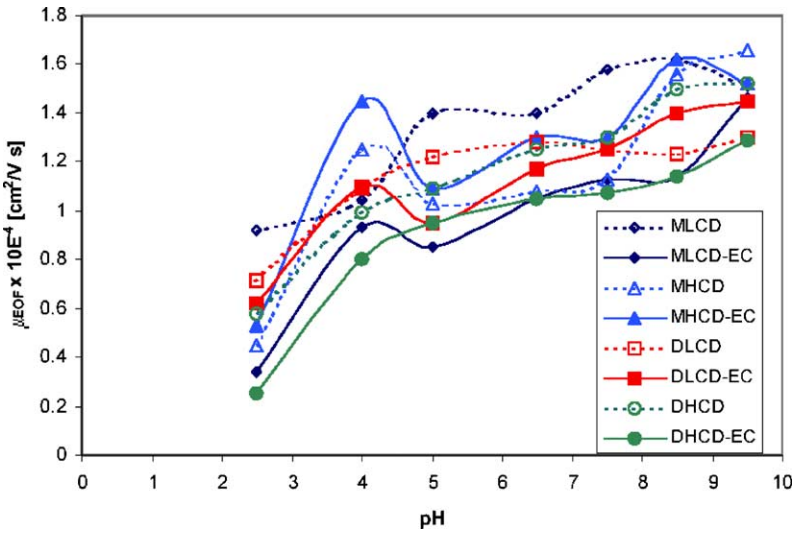

Fig. 1. EOF profiles obtained on C_{18} phases of different coverage density. Experimental conditions: mobile phase ACN–buffer (70:30), $c = 5$ mM; buffers: phosphate pH 2.5, 6.5, 7.5, acetate pH 4.0 and 5.0, Tris pH 8.5, borate pH 9.5. $U = 20$ kV, injection 5 kV for 3 s. Test solute: thiourea (t_0); detection at 254 nm. For packing abbreviations, see legend to Table 2.

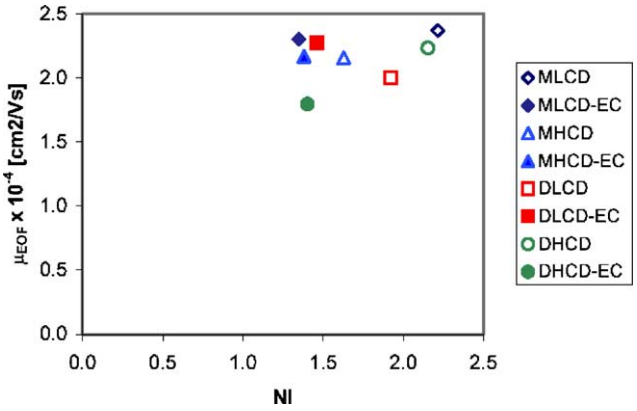

Fig. 2. Electroosmotic mobility vs. silanol activity (NI) for C_{18} phases of different coverage density. Experimental conditions: mobile phase ACN–Tris pH 8.5 (70:30), $c = 5$ mM. Test solutes: thiourea (t_0), phenol and aniline; detection at 200 nm. For packing abbreviations, see legend to Table 2.

decided to follow the work of Jiskra et al. [11] who applied the Galushko test [12] to evaluate differences between behaviors of the stationary phase under HPLC and CEC conditions. In the Galushko test [12], silanol activity (NI) is determined using retention data of aniline and phenol:

$$\mathrm{NI} = 1 + 3\left(\frac{k_{\mathrm{aniline}}}{k_{\mathrm{phenol}}} - 1\right). \quad (3)$$

Because of some problems with the in-column detection of phenol and aniline occurred, we decided to continue experiments with traditionally packed columns (25 cm of packed segment +8.5 cm of open segment). The EOF velocities generated on such columns were higher; however, the problem of bubble formation was occasionally disturbing experiments.

The results presented in Fig. 2 show that not end-capped stationary phases generated higher EOF with the increase in NI. However, NI is not correlated with the carbon content or surface coverage (Table 2). For example, the stationary phase denoted as DHCD ($\alpha_{\mathrm{RP}} = 3.64\,\mu\mathrm{mol/m^2}$) is characterized by higher values of NI and μ_{EOF} than DLCD ($\alpha_{\mathrm{RP}} = 3.27\,\mu\mathrm{mol/m^2}$). These observations are, to some extent, in agreement with the results obtained by Tanigawa et al. [13] who observed higher electroosmotic mobilities for polymeric phases of higher coverage density. They also reported higher μ_{EOF} for polymeric than for monomeric C_{18} chemically bonded phases. The explanation was that octadecyltrichlorosilane, which was used by these authors for silica modification (or octadecylmethyldichlorosilane used in our study), leaves one or two chlorine atoms that cause silanol regeneration after contact with water. End-capped materials exhibited similar values of NI and μ_{EOF}, except the DHCD-EC phase, which is characterized by the highest coverage density ($\alpha_{\mathrm{RP}} = 3.71\,\mu\mathrm{mol/m^2}$) and it is end-capped (EC), so the access of the molecules to the silica surface was strongly limited.

The increasing content of the organic modifier in the mobile phase resulted in faster EOF, up to $\mu_{\mathrm{EOF}} \sim 2.5\,\mathrm{cm^2/(V\,s)}$ for most of the stationary phases (Fig. 3). Simultaneously, NI increased, however, NI of not end-capped materials differed strongly and gave a much steeper rise (Fig. 4). It seems that these observations can be explained in such a way that alkyl chains become more extended with a decrease of water content in the mobile phase. Hence, the access of molecules of the buffer and test analytes to the silica surface is less limited. However, it does not make the EOF much faster (Fig. 4). According to Eq. (1) the EOF depends on zeta potential as well as on the $\varepsilon_{\mathrm{L}}/\eta$ ratio of the mobile phase. Assuming constant ζ, the increase in the $\varepsilon_{\mathrm{L}}/\eta$ ratio makes the EOF faster. The above-mentioned results show that extending the alkyl chain and uncovering the silica surface do not increase the zeta potential. Moreover, it can be assumed that for the majority of stationary phases ζ has almost the same value. According to the literature data [14], the zeta potential decreases with an increasing

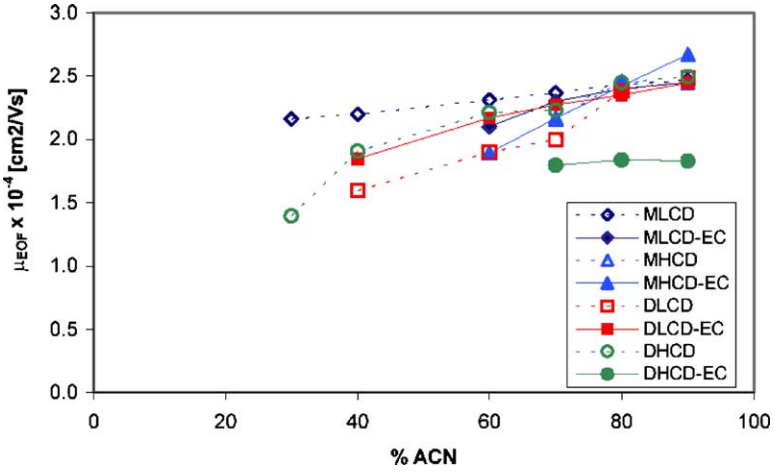

Fig. 3. Changes of the electroosmotic mobility with acetonitrile content in the mobile phase obtained for C_{18} phases of different coverage density. Experimental conditions: mobile phase acetonitrile–Tris pH 8.5, $c = 5$ mM. Test solute: thiourea (t_0); detection at 200 nm. For packing abbreviations, see legend to Table 2.

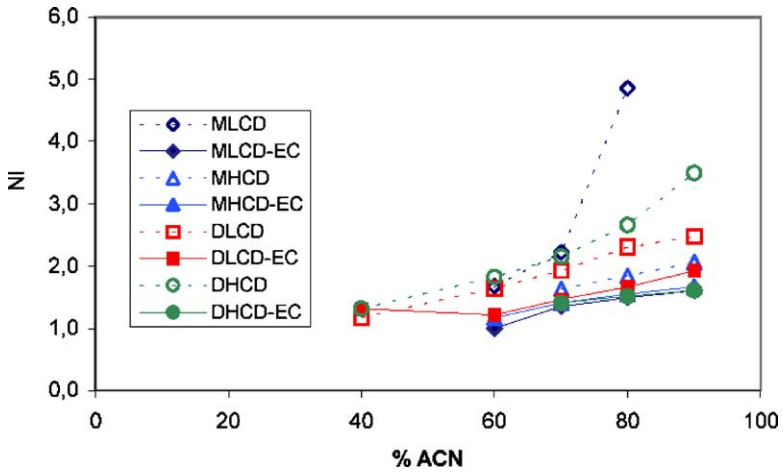

Fig. 4. Changes of the silanol activity with acetonotrile content in the mobile phase obtained for C_{18} phases of different coverage density. Experimental conditions as in Fig. 3. For packing abbreviations, see legend to Table 2.

content of the organic modifier in the buffer/mobile phase. On the other hand, Dearie et al. [15] reported that for Spherisorb C_{18} stationary phase the zeta potential did not change significantly (17–20 mV) with an increase in the acetonitrile amount (30–80%, v/v) in the mobile phase. For lower content of the organic modifier μ_{EOF} decreases but differently for the described adsorbents. These observations confirm the theory proposed by Dearie et al. [15] that for the ACN content lower than 40–50% ζ is responsible for the EOF velocity. A rapid decrease in μ_{EOF} in the range of 90–60% ACN (e.g. for MHCD and MLCD-EC phases) may be a proof that for these materials EOF depends primarily on the ε_L/η ratio. It should be also noted that for the MLCD phase (characterized by the lowest coverage density— C (%) = 10.66, α_{RP} = 1.75 μmol/m^2) μ_{EOF} decreased by 6% only. This disagrees with the results obtained by Tanigawa et al. who observed a 30% decrease in μ_{EOF} when the ACN content changed from 90 to 70%, although they used a very similar stationary phase (C (%) = 8.2, α_{RP} = 1.0 μmol/m^2). Such drastic differences may be explained by differences in stationary phase characteristics, for example S_{BET}, the concentration of impurities, and homogeneity of the surface coverage.

3.3. EOF on alkylamide phases

Buszewski and coworkers introduced alkylamide phases (AP) as new generation packings for HPLC [7,8]. AP packing materials are obtained during a two-stage synthesis, which is schematically presented in Fig. 5.

Alkylamide phases possess three kinds of polar functional groups: residual silanols (ca. 32%), residual aminopropyl groups (ca. 29%) and alkylamide groups (ca. 39%). The possibility of the application of AP phases to CEC depends on how fast EOF they can generate. Initially we tried to perform experiments with traditionally prepared columns (packed segment + open segment) but because of drastic differences between electroosmotic mobility generated by these two parts of the capillary it was impossible to generate the flow. For most of the AP phases tested, in fully packed capillary columns the EOF could be generated after 2–3 days of flushing the capillary with the mobile phase consisting of acetonitrile and phosphate buffer with pH 2.5. It indicates relatively slow protonization of amine groups during this step of column conditioning. After EOF stabilization at pH 2.5 consecutive experiments were performed in the same way as for C_{18} column.

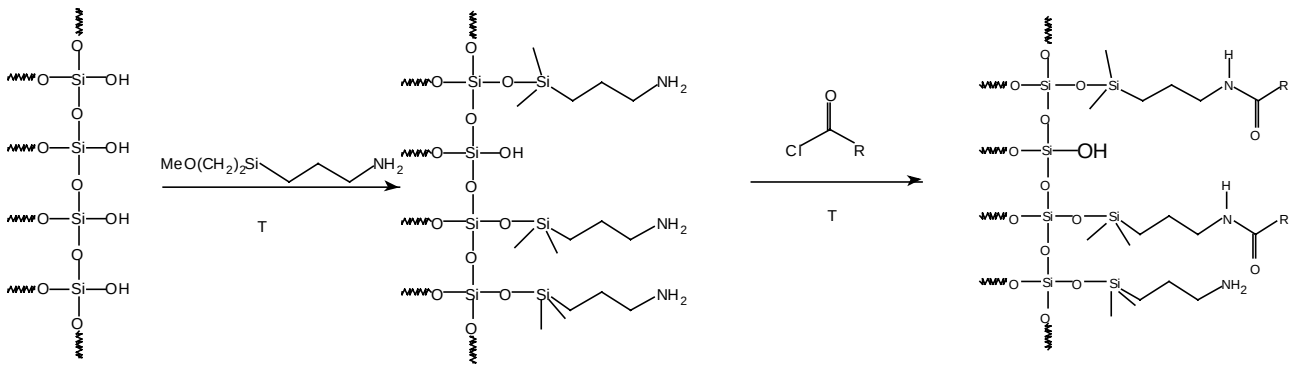

Fig. 5. Scheme of syntesis of alkylamide phases, where R stands for alkyl chain.

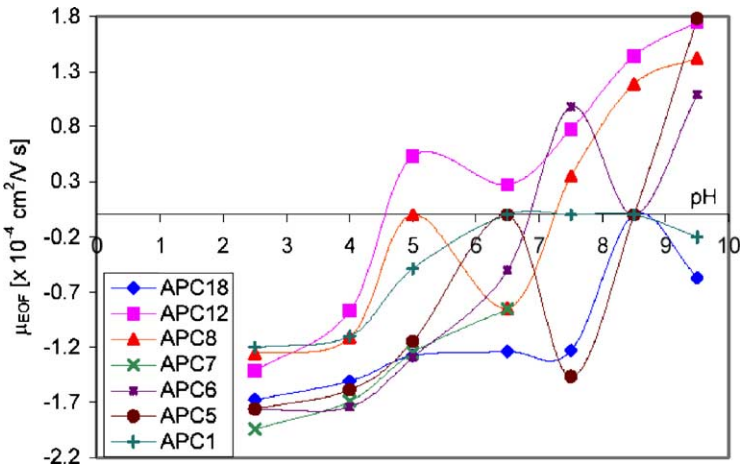

Fig. 6. EOF profiles obtained on alkylamide phases with different alkyl chain length. Experimental conditions: mobile phase ACN–buffer (70:30), $c = 5$ mM; buffers: phosphate pH 2.5, 6.5, 7.5, acetate pH 4.0 and 5.0, Tris pH 8.5, borate pH 9.5. $U = \pm 20$ kV, injection ± 5 kV for 3 s. Test solute, thiourea; detection at 254 nm.

The EOF profiles of the AP phases with alkyl chain of different lengths ($n_c = 1, 5, 6, 7, 8, 12, 18$) are presented in Fig. 6. For these materials, the presence of positively charged groups (amine and amide) is responsible for the EOF generation at low pH (2.5–5) values. The direction of EOF is, therefore, reversed in comparison with negatively charged silica materials. An increase in pH value should reverse the EOF, because of silanol dissociation and deprotonization of the amine groups. Bartle et al. [16] who observed a "symmetrical" EOF profile for the aminopropyl phase reported such a phenomenon. It means that the linear velocities of the mobile phases were almost identical at low pH (2–4) and at high pH (7–8), but the directions of the flow were opposite. The change of the EOF direction was observed at the pH range 5–7.

The AP materials described behaved similarly, i.e. they generated EOF at both directions, dependently on pH. Such observation may suggest that AP phases can be used at both low and high pH. However, it should be noted that the AP-C_{18} phase generated only reversed EOF (negative μ_{EOF} values). This may indicate:

(i) lack of silanols in this phase or, more probably, their marginal influence, and/or:
(ii) slow deprotonization of amine groups with increasing pH.

Moreover, we observed the phenomenon of EOF deterioration at pH 8.5 and 9.5. First, at low pH, the electroosmotic mobility of the AP phases was negative. Increasing the pH made EOF slower, then the direction reversed to opposite (positive μ_{EOF} values), and, for most phases, the velocity of the mobile phase increased. This fact proved the presence of a negative surface charge on these materials. These μ_{EOF} values are presented in Fig. 6. However, on continuation of CEC experiments at high pH we observed that EOF velocity gradually decreased to zero and, in some cases, it changed the direction (see Fig. 6).

At neutral pH, i.e. 5–7.5, the gradual dissociation of silanols and deprotonization of amine groups should take place. In this range, the electroosmotic mobility depends on the resultant charge during a given experiment. That is why some of the EOF profiles are surprising (for example AP-C_5 or AP-C_8 phases).

Some differences in electroosmotic mobility of different AP phases are especially noticeable at low pH (2.5–4.0) of the mobile phase. This is probably connected with different concentrations of residual aminopropyl groups after second step of the synthesis (Fig. 5).

If the velocity of the electroosmotic flow depends on the availability of terminal polar groups on the silica (see considerations in previous sections), the increasing length of the alkyl chain should make this access more difficult, especially with a low content of the organic modifier in the mobile phase (chain collapse). The relationships between the acetonitrile content and electroosmotic mobility observed for AP phases differ from these above-discussed for C_{18} packings (Fig. 7). Here, a slight increase in μ_{EOF} (max. 0.65 $cm^2/(V\,s)$ for the AP-C_8 phase) or almost constant mobility (e.g. for the AP-C_5 phase) are observed when the acetonitrile content changes from 40 to 80%. Moreover, these changes are not connected with the chain length except for the AP-C_1 phase. These effects we attribute to the presence of a *hydrolytic pillow* on the silica surface. Buszewski and coworkers [17–19] observed enhanced sorption of water from hydro-organic mobile phases by alkylamide packings. The authors reported that the presence of polar groups (silanols, amine and amide) is responsible for this phenomenon. Under HPLC conditions (no buffer in the mobile phase) the *pillow* hinders the access of polar solutes to the silica surface [19,20]. Hence, it is possible, that under CEC conditions (mobile phase contains buffer) the zeta potential is not created on the silica surface but on the border of the *hydrolytic pillow* and hydro–organic mobile phase. However, more experimental data are needed

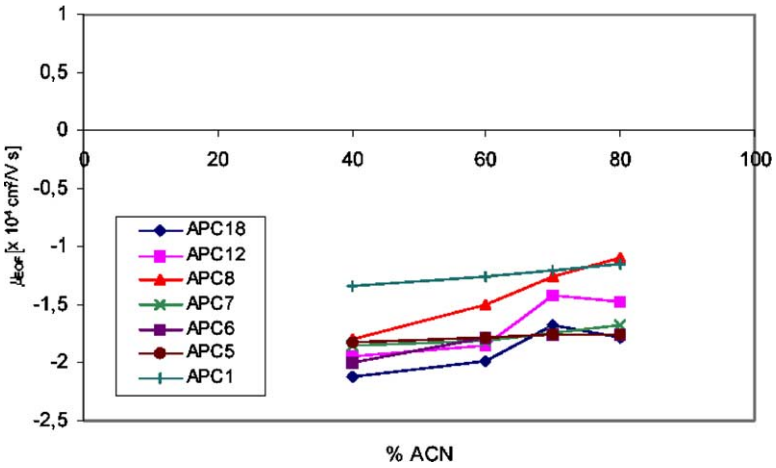

Fig. 7. Changes of the electroosmotic mobility with acetonotrile content in the mobile phase obtained for alkylamide phases with different alkyl chain length. Experimental conditions: mobile phase acetonitrile–phosphate pH 2.5 (70:30), $c = 5$ mM. $V = -20$ kV; test solute: thiourea (t_0); detection at 254 nm.

for better understanding of these processes. It is very likely, that the EOF deterioration under high pH conditions may be attributed to the *reorganization* of buffer and solvent molecules between silica surface and amine/amide groups (top of the *pillow*) (Fig. 8). Probably this process required some time, however, it was difficult to describe it quantitatively. Each change of the buffer disturbed this equilibrium.

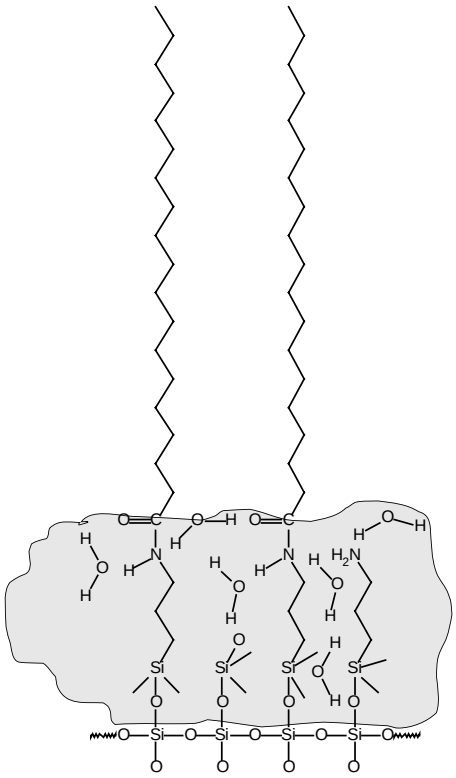

Fig. 8. Scheme of *hydrolytic pillow* that is formed on alkylamide phases. The presence of polar groups enhances the sorption of water because of hydrogen bonding.

4. Conclusions

The studies performed on the specially synthesized stationary phases show that there is no direct correlation between silanol activity and the electroosmotic flow generated. Relatively high electroosmotic mobility observed at low pH may be a good indicator of silica impurity. On the one hand, the presence of impurities in silica worsens the quality of this material in liquid chromatography, being the source of undesired interactions. On the other hand, it enables EOF generation at low pH, however much better results can be obtained on ion-exchange materials described, e.g. by Smith and Evans [21].

The results obtained for alkylamide phases confirmed, to some extent, the hypothesis of the *hydrolytic pillow*, but some more detailed experiments are needed in this field. Surprisingly, the nitrogen containing materials cannot be *bi-directional* phases because of the EOF deterioration at high pH conditions.

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