Journal of Chromatography, 602 (1992) 227–234
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2539

Bonded-phase capillaries and the separation of inorganic ions by high-voltage capillary electrophoresis

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ABSTRACT

Both a C_1 and a C_{18} saturated hydrocarbon have been bonded to 75-μm capillaries for high-voltage capillary electrophoresis separations. The performance of these bonded phases has been compared with unbonded capillaries under a variety of experimental conditions. The bonded phases were prepared by a flow-through procedure at room temperature, and the reproducibilities of the electroosmotic flow for the C_1 and C_{18} capillaries were 6 and 3%, respectively. Both of the bonded phases reduced interactions between the silica surface and positively charged ions, but for larger hydrophobic ions sorption and peak tailing were observed on the C_{18} phase. In the presence of sodium dodecylsulfate and sodium decanesulfonate it was possible to control the electroosmotic flow over a wide range. The separation of lanthanide metal ions is illustrated, and improved resolution and reduced surface interactions are shown for the bonded phases.

INTRODUCTION

High-voltage capillary electrophoresis (CE) is a technique for the separation of charged species in small capillaries at electric field strengths in the range of 10 to 30 kV. The small-diameter capillaries dissipate heat efficiently and can provide very efficient separations. This technique is growing rapidly, and has been the subject of several recent review articles [1–3]. Fused-silica capillaries have been used widely in CE. Since the walls of silica capillaries are normally negatively charged in aqueous solution from the ionization of surface silanol groups, positive counterions are present in the double layer adjacent to the capillary walls. Some of these counterions induce a flow at the wall, and as long as the capillary is small, all of the liquid in the capillary will flow with these ions. This flow is termed electroosmotic (EO) flow, and it has a flat velocity distribution across the capillary, except for a few nanometres at the capillary surface [4,5]. Thus the net rate of elution of any ion is the sum of the EO flow and the electrophoretic mobility of the ion; neutral compounds will be carried at the velocity of the EO flow. Therefore, the rate of electroosmotic flow can affect separation time and resolution [1]. The chemical properties of the interface can also affect analyte sorption, which results in band broadening, and in some cases the peak is lost completely. Thus it would be useful to have the ability to control the chemial and physical properties of the silica–electrolyte interface.

The majority of CE separations have been performed in untreated fused-silica capillaries. Untreated capillaries can sorb solutes by electrostatic and/or chemical interactions, especially in the case of large molecules like proteins. Several research groups have tried to eliminate adsorption by coating the capillary wall with a polymer, or by covalently bonding organic phases to the surface. The composition of surface phases used to reduce protein sorption have included the following: methylcellulose [6], acrylamide [7,8], trimethylsilane [9], epoxydiols [10], maltose [10], polyethylene glycol [11,12], poly(vinylpyrrolidine) [13], arylpentafluoro [14], polyethyleneimine [15], OV-1 [16], and Carbowax 20M [16]. Recently, commercially-prepared bonded phases have been introduced, but, to a large part, the properties of these phases are proprietory information [17]. In addition to the reduction of the

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sorption of proteins, the goal of several studies of surface treatment has been to reduce EO flow [12]. In large capillaries this is required to reduce band broadening due to parabolic flow [12]. For smaller diameter capillaries elimination of EO flow will maximize resolution arising from differences in electrophoretic mobilities. The most effective coatings for elimination of EO flow have been large molecules, such as methylcellulose [6], acrylamide [7] [8], polyethylene glycol [11,12] and poly(vinylpyrrolidine) [13].

Another way to manipulate EO flow is via surfactant interaction. When surfactants are added to the electrolyte, even at concentrations below the critical micelle concentration, they adsorb at the surface of the capillary. This adsorption changes the surface properties and can have dramatic effects on the separation. Altria and Simpson [18] briefly studied the effect of cationic surfactants, with carbon chain lengths from 1 to 16, on the EO flow, and found that the flow decreased linearly with the log of surfactant concentration. Other studies [19,20] have used cationic surfactants to reverse the electroosmotic flow for the separation of anions. Foret *et al.* [21] have used a non-ionic surfactant to eliminate electroosmotic flow. In principle, only cationic and non-ionic surfactants adsorb sufficiently on the silica surface to be of practice use; presumably, anionic surfactants are repelled by the negative charge of the dissociated silanol groups. However, if the surface is first bonded with a hydrophobic phase, the anionic surfactant will sorb on the surface by hydrophobic interaction. In practice, all types of surfactants should sorb onto the surface, hopefully to an extent that can be reproducibly controlled by the concentration of the surfactant in the electrolyte and by the electrolyte composition. Thus it should be possible to quickly evaluate the effects of different surface loadings and different charge densities on the performance of the capillary for a variety of surfactants. In the studies here, sodium dodecylsulfate (SDS) and sodium decanesulfonate (SDECS) have been used to manipulate EO flow on three types of capillaries: unbonded, a highly-hydrophobic bonded phase, and a weakly-hydrophobic bonded phase.

The lanthanide series of metal ions is one of the classes of ions that we have chosen to evaluate these bonded-phase capillaries. Lanthanides are of importance in nuclear science, high-efficiency magnets, and as geological tracers. Efficient separation processes are important for these metal ions, and liquid chromatographic techniques have been employed for this purpose [22–25]. Although capillary electrophoresis has become accepted for the separation of organic species, the separation of inorganic compounds has not gained widespread acceptance [26]. Recently, Foret *et al.* [26] separated lanthanides with a polyacrylamide coated capillary, with α-hydroxyisobutyric acid (HIBA) as a selective complexing counterion and creatinine for indirect UV detection. The purpose of the present studies was to evaluate the potential of surfactants and bonded phase with lanthanides as the test solute ions.

EXPERIMENTAL

Apparatus and electrophoresis

A Waters Quanta 4000CE system (Millipore Waters, Milford, MA, USA) equipped with a positive high-voltage power supply was used. Polyimide-coated fused-silica capillaries, 60–70 cm in length with an I.D. of 75 μm, were obtained from Polymicro Technology (Phoenix, AZ, USA). The window of the on-column detector cell was created by burning a small section (*ca.* 0.5 cm) of the polyimide-coating off with a match, and excess residue was then wiped off with methanol or acetone. The sample was injected hydrostatically with the capillary inlet lifted 9.8 cm higher than the capillary outlet for a few seconds. The electrolyte was monitored at 214 nm. The electropherogram was recorded and evaluated on a PC computer with a Waters SIM interface and Waters Baseline 820 software.

Chemicals

All solutions were prepared from water that was distilled, deionized and then distilled again (Corning Mega-Pure system, MP-6A & D2; Corning, NY USA). The stock acetate buffer was prepared by mixing two acetate buffers that had different pH values but the same total concentration of acetate, to give the final desired pH value of 4.6. This buffer always contained a total concentration of free acetate of 0.01 mol/l. The pH was measured with a combination glass electrode calibrated with pH 4.0 and 7.0 buffers (Hydrion dry buffers; Aldrich, Mil-

waukee, WI, USA). The electrolytes containing surfactants were obtained by mixing the stock acetate buffer with a 0.01 mol/l stock solution of the surfactant; SDS (99%; Sigma, St. Louis, MO, USA) or SDECS (98%, Aldrich). This approach gave a constant ionic strength if the volume change on mixing was negligible. All surfactant solutions were at concentrations below the critical micelle concentration. The background electrolyte for lanthanide separations was 9 mmol/l benzylamine (BDH, Toronto, Canada), 4 mmol/l hydroxyisobutyric acid (98%, Aldrich) and 20 mmol/l acetic acid (BDH). The pH value of this solution was 4.60. The benzylamine (BDH) was purified by distillation under vacuum. All solutions were filtered through a 0.2-μm nylon-66 membrane syringe filter (Cole-Parmer, Chicago, IL, USA) prior to use.

Samples of $1.0 \cdot 10^{-4}$ mol/l benzylalcohol (analytical reagent, BDH) were used to determine the EO flow. Benzyltrimethylammonium chloride was reagent grade (97%, Aldrich). Lanthanide samples were obtained from Alfa (Danvers, MA, USA) as nitrate salts (Dy, Er, Gd, Ce), chloride salts (La, Pr, Yb) and as oxides (Nd, Sm, Lu, Tm, Ho, Eu). Oxides were dissolved in an excess of 0.5 mol/l nitric acid, evaporated to dryness, and redissolved in water to form a 0.01 mol/l stock solution. Test samples ($1.0 \cdot 10^{-4}$ mol/l) were prepared by dilution of 20 μl of the 0.01 mol/l stock solution to 2 ml in the electrolyte. All injected samples were filtered through a 0.2-μm nylon-66 membrane syringe filter prior to injection. The trimethylchlorosilane (99.9%) and dimethyloctadecylchlorosilane were obtained from Hüls Petrarch Systems (Bristol, PA, USA). Imidazole (99%, Aldrich) was dried under vacuum ($\approx$20 mmHg) for two days. The reaction solvents, N,N-dimethylformide (DMF, certified ACS, Fisher) and dichloromethane (analytical grade, BDH) were distilled over calcium hydride 2 h prior to use.

Preparation of bonded phases

The capillaries were etched with 1.0 ml/l sodium hydroxide for 3 h at room temperature, rinsed with water for 10 min, flushed overnight with 1.2 mol/l hydrochloric acid to remove Na^+ from wall and to produce free silanol groups, washed with water for a few hours to remove excess acid, rinsed with methanol for 0.5 h, and then dried at 160°C for 3 h by gentle flushing with nitrogen.

A schematic of the arrangement used for the preparation of the bonded phases is shown in Fig. 1. Solutions of trimethylchlorosilane in dried DMF or dimethyloctadecylchlorosilane in dried dichloromethane were prepared in 1.5-ml polypropylene centrifuge tubes (Cole-Parmer); dried imidazole was added as an acid acceptor. The concentration of the silane (0.01 mol/l) in one capillary volume was over five times higher than that required for complete coverage of the surface silanols in one capillary, and the concentration of the base was double the concentration of the silane [27]. These reactant mixtures were filtered through a 0.2-μm nylon-66 membrane syringe filter into antoher centrifuge tube, and a 100-μl eppendorf pipette tip was inserted into the cap of the tube (Fig. 1). The capillary was inserted through the pipette tip into the solution, and a small cotton ball was put around the capillary in the bottom of the tip, followed by calcium chloride and more cotton to cover on the top of the calcium chloride. The silane solution with the capillary inserted was held to a height of *ca.* 30 cm above the other end of the capillary. The silane solution was sucked through the dried capillary with a syringe connected with a length of polyethylene tube (I.D. 0.38 mm), and the solution was allowed to run through the capillary by gravity (see (Fig. 1)

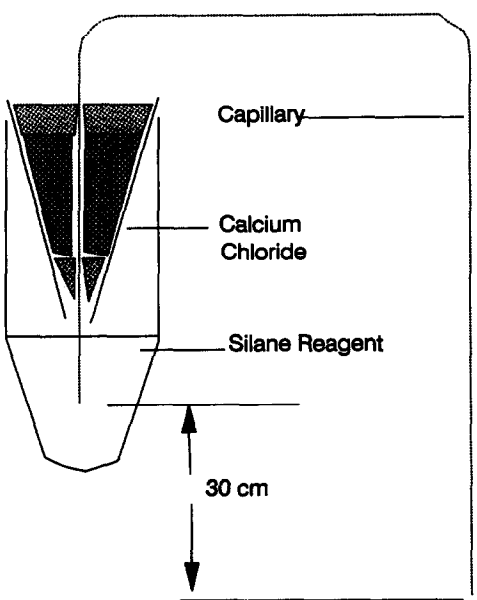

Fig. 1. Apparatus used for bonding capillaries.

for 24 h. After reaction, each capillary was rinsed with the pure reaction solvent (DMF for C_1 and dichloromethane for C_{18}), followed by methanol, water, and then with the aqueous buffer overnight.

Preparation of Carbowax 20M-coated capillary

The procedure used for coating the capillary with Carbowax 20M was based on procedures reported for liquid and gas chromatographic packings [28,29]. The capillary was washed with 1.0 mol/l hydrochloric acid for 3 h, rinsed with water for 0.5 h, and methanol for 0.5 h. The capillary was then dried at 150°C by gentle flushing with nitrogen for 3 h, filled with a 6% (w/w) Carbowax 20M chloroform solution, connected to a gas chromatograph, flushed with nitrogen at 50°C for 3 h, and then at 270°C for 16–18 h. The capillary was then washed with methanol, filled with the aqueous buffer and allowed to stand overnight.

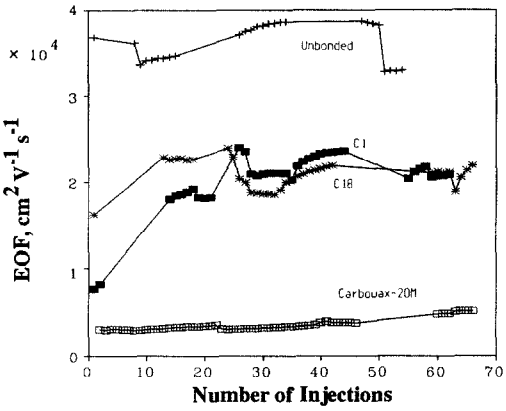

Fig. 2. The electroosmotic flow (EOF) coefficient as a function of number of injections. Experimental conditions: 9 mmol/l benzylamine, 4 mmol/l HIBA and 20 mmol/l acetic acid at pH 4.60; electric field, 460 V/cm; injection, 6 s at a differential height of 9.8 cm.

RESULTS AND DISCUSSIONS

Preparation of bonded phase

The first preparation tried was a 24-h reaction in an ultrasonic bath [30], but it was difficult to seal the capillary, and the temperature of the water in the bath rose to 50°C, which caused bubbles to form in the capillary. Even with the higher-boiling solvent, DMF [31], it was found that this procedure was too complicated. Since Jones [32,33] had shown that the yield of the silanization did not appreciably change from room temperature to reflux, a room temperature reaction was used with the silane solution flowing through the capillary overnight. Imidazole was chosen as the acid acceptor because a study of several organic bases showed [31] that it gave the fastest reaction rate. The bonding procedure was repeated three times (3 × 24 h) on the same capillary, and it was found that the EO flow did not change when reaction times above 24 h were used. Consequently, all capillaries were made to react for 24 h.

Stability and reproducibility of bonded and unbonded capillaries

The EO flow was monitored with the uncharged molecule, benzylalcohol ($1.0 \cdot 10^{-4}$ mol/l) at pH 4.60 for bonded and unbonded capillaries for a total of up to 65 injections (shown in Fig. 2), and it was found that the EO flow was essentially stable after 12 injections. The electroosmotic flow for both the C_1 and C_{18} phases was decreased by about 35% relative to that for the unbonded capillary, which is similar to that reported for a commercially available bonded phase [17]. The Carbowax 20M coating gave a very low EO flow, but there was a slight increase with time, indicating a possible slow loss of the polymer. The portions of the curves in Fig. 2 that do not have data points represent periods when the capillary was used for other tests with electrolytes containing surfactants. At the end of each of these test periods the capillaries were washed with acetonitrile–water 1:1 overnight, and then placed in the acetate buffer. The curves in Fig. 2 show that this rather drastic change in elecrolyte composition could be made with little change in EO flow. To achieve this reproducibility, however, careful attention had to be given to the purity of the solutions and the treatment of the containers used. During initial studies large and irreproducible variations in EO flow were observed when different batches of electrolytes of the same composition were used (even in the absence of surfactants). It was eventually found that the changes in EO flow could be controlled if all materials were cleaned in alcoholic potassium hydroxide and the use of soaps to clean containers was eliminated. Such irreproducible behaviour is not uncommon in CE and this behaviour

TABLE I

AVERAGE ELECTROOSMOTIC FLOW COEFFICIENT AND ITS STANDARD DEVIATION ON C_1 AND C_{18} CAPILLARIES

The electrolyte is an acetate buffer (acetate concentration of 0.01 mol/l) with a pH of 4.60, and the electric field is 500 V/cm.

No.	Capillary	Number of measurements	Average of EOF ($cm^2V^{-1}s^{-1}$)	R.S.D. of EOF (%)
1	C_{18}	19	$2.27 \cdot 10^{-4}$	13
2	C_{18}	20	$2.23 \cdot 10^{-4}$	4.4
3	C_{18}	20	$2.36 \cdot 10^{-4}$	12
4	C_1	20	$2.35 \cdot 10^{-4}$	11
5	C_1	20	$2.09 \cdot 10^{-4}$	6.9
6	C_1	20	$2.30 \cdot 10^{-4}$	10
Average of capillaries 1–3			$2.29 \cdot 10^{-4}$	3
Average of capillaries 4–6			$2.25 \cdot 10^{-4}$	6

is likely caused by the sorption of small amounts of impurities onto the capillary surface.

To evaluate the reproducibility of the chemical bonding procedure, three capillaries were treated with C_1 and C_{18} reagents. The average EO flow coefficient and the standard deviation for each of the capillaries are shown in Table I. The standard deviations of the EO flows for the capillaries ranged from 4 to 13%; much larger deviations were observed if proper experimental procedures were not maintained (see above). The relative standard deviations for the results between individual capillaries was considered to be very good, at 3% and 6% for C_1 and C_{18} bonded phases, respectively (see Table I). These results show that the procedures used in this study can produce reproducible bonded phases.

The ability of the bonded phase to shield cations from interactions with the silica surface of the capillary was also studied briefly with the organic cation, benzyltrimethylammonium chloride. Although it is difficult to make an absolute comparison because of differences in EO flows and elecrolyte composition, the results indicated that the C_1 bonded phase had the best shielding properties, with a peak symmetry (peak-tail/peak-front) of 2.9. The peak symmetry for the unbonded phase was 4.9, and for the C_{18} phase, 4.3. The large value for the C_{18} phase is likely due to hydrophobic interactions as this broadening was not observed with inorganic cations.

Effect of the ionic strength on electroosmotic flow and column efficiency

It is known that EO flow decreases with an increase in ionic strength on unbonded capillaries, due to changes in the thickness of the charged double layer at the capillary–electrolyte interface [34]. While the structure of the double layer is uncertain for bonded phases, the presence of salts still can affect EO flow as shown by the results in Fig. 3. Column efficiencies (HETP) for benzylalcohol as a function of ionic strength of the electrolyte for bonded and unbonded capillaries are shown in Fig. 4. The column efficiency decreased with ionic

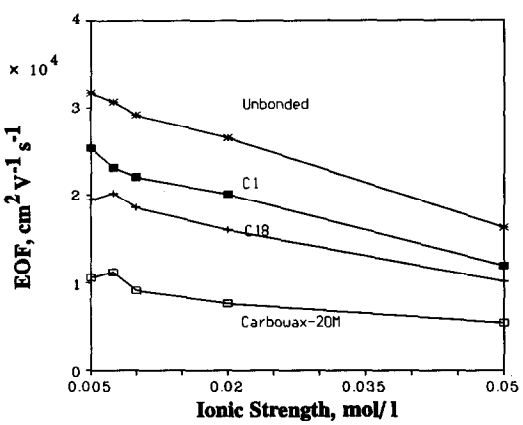

Fig. 3. The electroosmotic flow (EOF) coefficient as a function of ionic strength. Experimental conditions: acetate buffer at pH 4.60; electric field, 200 V/cm; injection time, 6 s.

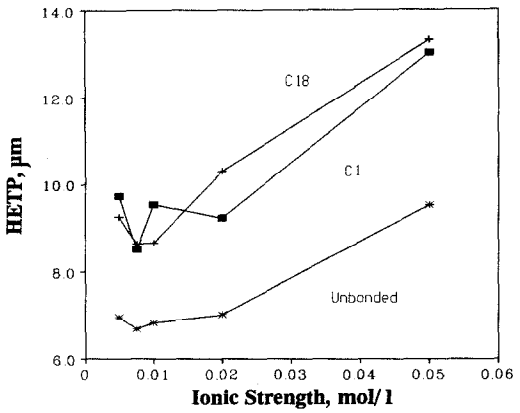

Fig. 4. Column efficiency as a function of ionic strength. Experimental conditions as in Fig. 2. Test solute is $1 \cdot 10^{-4}$ mol/l Ce (III).

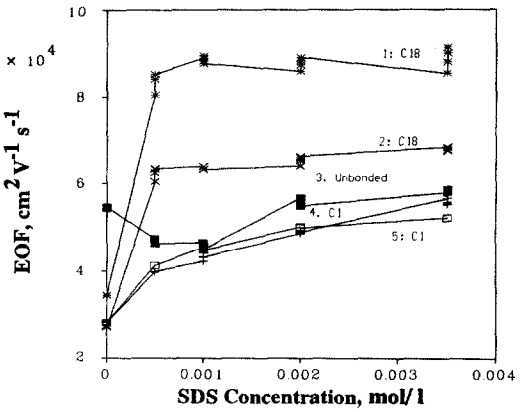

Fig. 6. The electroosmotic flow coefficient as a function of concentration of SDS. Experimental conditions as for Fig. 5.

strength, and this was primarily due to an increase in longtitudinal diffusion with longer separation times.

Effect of anionic surfactants on the electroosmotic flow on the bonded and unbonded capillaries

When capillary surfaces are bonded with hydrophobic phases, hydrophobic anionic surfactants can be adsorbed on the surface. Since the EO flow is inversely proportional to the ionic strength, the effect of different concentrations of SDECS and SDS surfactants was studied at constant ionic strength. The results in Fig. 5 and Fig. 6 show that it is possible to control the EO flow over a wide range by the addition of surfactants to electrolytes used in bonded-phase capillaries. The EO flow in the unbonded capillary was not appreciably affected by the presence of the negatively charged surfactants. This is expected due to the negatively charged surface of the silica surface. All of the bonded phases exhibited an increase in EO flow as surfactant was added, but for the C_1 phase this was only appreciable for the longer-chain surfactant. Only in the case of the C_{18} phase was it possible to surpass the EO flow of the unbonded capillary, and as the surfactant was added the EO flow increased quickly to reach a plateau value, presumably caused by saturation of the surface with the surfactant. Both of the C_1 capillaries exhibited similar EO flow patterns. However, for the C_{18} capillaries quite different flow-rates were observed. Since EO flow is sensitive to small changes in the composition of the interface, it is possible that small changes in bonding density for the C_{18} phase will affect the sorption of surfactant to a greater extent than for C_1 phases.

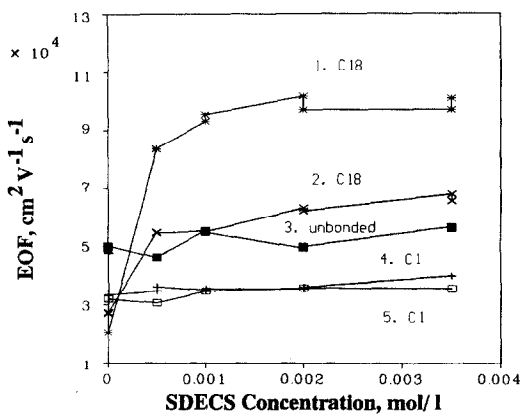

Fig. 5. The electroosmotic flow coefficient as a function of concentration of SDECS. Experimental conditions: acetate buffer with ionic strength 0.01 mol/l and pH 4.60; electric field, 200 V/cm; other condition as for Fig. 2.

Lanthanide separations on the bonded and unbonded capillaries

Lanthanide separations on C_{18} and C_1 capillaries were obtained with an electrolyte containing 4 mmol/l HIBA, 9 mmol/l benzylamine and 20 mmol/l acetic acid; benzylamine was used for indirect detection. The separations for a C_{18} and an unbonded capillary are shown in Fig. 7. The C_{18}

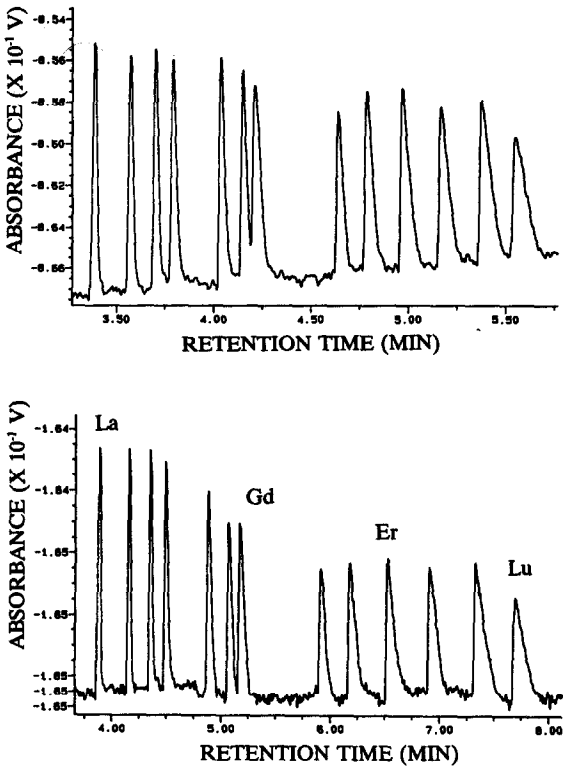

Fig. 7. Electropherogram of lanthanide separation on the C_{18} (bottom) and unbonded capillaries (top). Experimental conditions: concentration of lanthanides is $1.0 \cdot 10^{-4}$ mol/l; detection at 214 nm; other conditions as for Fig. 1.

phase seems to show a slightly enhanced separation with the resolution of Eu(III) and Gd(III) being 1.2 on the C_{18} capillary and 0.81 on the unbonded capillary. It should be noted that most lanthanides exhibit tailing peaks, which becomes worse at longer retention times. This broadening is not due to surface interactions, but is a result of differences between the electrophoretic mobilities of the analyte and elecrolyte ions. When the concentration of electrolyte is much larger that the concentration of analyte, or when the solute and the co-ion have close effective mobilities, symmetric peaks should be observed. This type of broadening can be worse in indirect detection, since the concentration ratio of background electrolyte to sample ion may be smaller than for direct detection methods. The electrophoretic mobility of protonated benzylamine is between Ce(III) and Pr(III), so that the Ce(III) peak is

TABLE II

HEIGHT EQUIVALENT TO A THEORETICAL PLATE (HETP) FOR LANTHANIDES

Lanthanide(III)	HETP (μm)		
	Polyamide [26]	C_{18}	Unbonded
La(III)		4.9	4.8
Ce(III)		3.9	4.6
Pr(III)		3.7	4.5
Nd(III)		4.2	5.2
Sm(III)		5.7	4.4
Eu(III)		5.2	4.6
Gd(III)		9.0	9.4
Tb(III)	10		
Dy(III)	12	6.9	5.8
Ho(III)	15	9.6	7.4
Er(III)	16	12.7	8.6
Tm(III)	18	13.5	9.8
Yb(III)	20	14	12
Lu(III)	28	18	16

expected to exhibit slight fronting and the later eluting ions are expected to tail. When the peaks were expanded it was found that the peaks for Ce(III) on the unbonded capillary tailed, but on the C_{18} and C_1 capillaries slight fronting was observed. This indicates that surface interactions are present in the separation of lanthanide cations in unbonded capillaries.

An initial comparison of the HETP values shown in Table II suggests that the overall column efficiencies for the C_{18} capillary are smaller than for the unbonded capillary. However, it is not possible to make a direct comparison because of the differences in retention time. The effect of band broadening processes will be related to the length of time spent in the capillary, and thus it may be more meaningful to compare peaks having similar retention time. If this is done in Fig. 7 it can been that the bonded phase exhibits improved efficiency, but even this comparison is not strictly correct. What is clear however, is that there is an improvement in resolution and a decrease in surface interactions. When these results are compared to those obtained on a polyamide coated capillary (see Table II) the results with the bonded phase were as good, if not better.

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