Characterization of quartz capillaries for capillary electrophoresis

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ABSTRACT

Different brands of commercially available quartz capillaries were investigated with respect to their optical and surface properties. Differences in inner diameter influence the detection sensitivity. Surface properties influence the electroosmotic flow (EOF). It is recommended to control the inner diameter and determine the EOF as a function of pH if new batches of capillaries are used. GC measurements and the dependence of retention on temperature permit one to characterize the coating procedure for non-polar coatings and to differentiate between polar and non-polar interactions. These values are in good agreement with measurements of the EOF and its dependence on pH.

INTRODUCTION

Although capillary electrophoresis (CE) has received wide application in recent years, so far no satisfactory method to characterize the surface of the capillaries has been described. Both systems, with the most widely used uncoated capillaries and also the coated capillaries, which are of growing importance [1–20], can only be characterized by the measurement of the electroosmotic flow (EOF) itself or its dependence on the pH of the applied buffer [4,21].

Stationary phases for HPLC or the coating of capillaries for GC are usually characterized by standard test procedures [22–24]. For the characterization of LC stationary phases, additionally a range of independent spectroscopic methods are available. The surface concentration of silanol groups can be determined easily [25]. Via the carbon content, the surface concentration of bonded groups can be calculated with good reliability.

The inner surface area of capillaries for CE with a usual length of less than 100 cm and an I.D. between 50 and 100 μm is of the order of a few square centimetres, hence the established methods cannot be used.

In addition to the magnitude of the EOF, mainly indirect methods for surface characterization are applied to the resulting effect, *e.g.*, the suppression of interactions of proteins with the surface wall [8,10–17]. To determine the layer thickness of a positively charged polyethylenimine coating, the adsorption of picric acid has been measured photometrically [17]. Non-polar and hydrophobic coatings have been characterized by GC measurements [19], and the layer thickness could be derived from the retention behaviour of *n*-nonane as a standard. In this paper, means for the characterization of uncoated and coated capillaries for CE are described by interpretation of the results of EOF measurements with quartz capillaries from different suppliers, and the combination of EOF and GC measurements to demonstrate the effectiveness of various coating procedures.

Correlation of EOF measurements with surface charges

In CE, the EOF is superimposed on the electrophoretic migration of charged species.

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The magnitude of the EOF depends, as an interfacial phenomenon, on the applied electric field E and on the distribution of charges in the interfacial layer. The latter is usually described as the zeta potential (ζ) [26]. The Helmholtz–Smoluchowski equation is

$$v_{eo} = -\frac{E\varepsilon_r\varepsilon_0}{\eta_0} \cdot \zeta \qquad (1)$$

where v_{eo} is the electroosmotic velocity (mm/s), ε_r the relative dielectric constant, ε_0 the dielectric constant in vacuum and η_0 the viscosity of the buffer solution. From this equation the zeta potential can be calculated. In Table I some typical values for CE are summarized. EOF values up to 4 mm/s are typical in CE. As can be seen, the calculated zeta potentials are in the range 1–100 mV. These values are in good agreement with published data [27] for electrolytes in contact with glass surfaces.

A mathematical correlation has been given [28] between the zeta potential and the specific surface charges at the boundary of the immobile double layer. These specific surface charges are a function of the charges on the quartz surface. The specific surface charge σ (in μC/cm^2) correlates with the zeta potential according to the equation [28]

$$\sigma = (8kT\varepsilon_r\varepsilon_0\eta_0)^{1/2} \sinh\left(\frac{ze\zeta}{2kT}\right) \qquad (2)$$

By inserting all the constants at 298 K, this equation becomes

$$\sigma = 11.7\sqrt{c^*} \sinh(19.5z\zeta) \qquad (3)$$

where z is the charge number, c^* the total concentration of the solution (mol/l) and the zeta potential is in volts. The electroosmotic mobility μ_{eo} (cm^2/V·s) is correlated with the specific surface charge by

$$\sigma = 11.7\sqrt{c^*} \sinh(2477.7z\mu_{eo}) \qquad (4)$$

(the numerical values given in Table I are used in this reduced equation).

In Fig. 1, the surface charge concentration, given in the usual measure of μmol/m^2, is plotted for the usual range of mobilities in CE in the range of $1 \cdot 10^{-4}$–$12 \cdot 10^{-4}$ cm^2 N·s.

The discussion of this curve is of great importance for the surface characterization of both uncoated and coated capillaries. Mobilities above $10 \cdot 10^{-4}$ cm^2/N·s are approached with quartz capillaries at pH values above 9. Here a surface charge concentration of 0.8 μmol/m^2 is calculated. If one assumes that all charges arise from dissociated surface silanols, the total concentration of silanol groups is almost an order of magnitude smaller than commonly accepted for silanol concentrations on crystalline quartz surfaces, for which values around 8 μmol/m^2 are calculated [25]. Two reasons for these differences can be discussed. The quartz capillaries are not totally hydrated owing to their production procedure. It is known from GC that the surfaces of quartz capillaries have to be "activated" prior to coating or bonding procedures by "leaching" and "etching" with sodium hydroxide, hydrofluoric acid, etc., to produce a sufficient number of active binding sites, i.e., silanol

TABLE I

CALCULATED ZETA POTENTIALS FOR DIFFERENT LINEAR VELOCITIES OF THE ELECTROOSMOTIC FLOW (ACCORDING TO EQN. 1)

Constants: $E = 40$ kV/m; $\eta = 10^{-4}$ Pa s (water at 25°C); $\varepsilon_0 = 8.854 \cdot 10^{-12}$ C^2 N^{-1} m^{-2}; $\varepsilon_r = 80$.

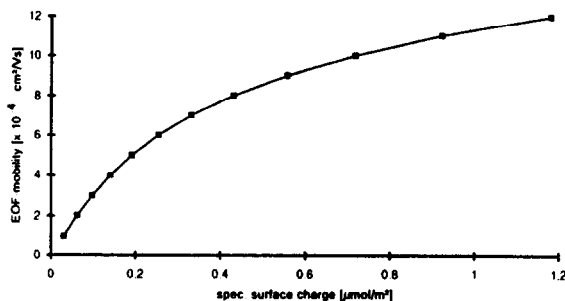| v_{eo} (mm/s)	ζ (mV)
0.1	3.1
1	31.7
2	63.5
3	95.2
4	127.0

Fig. 1. Relationship between the specific surface charge and electroosmotic mobility calculated for a 10 mM buffer according to eqn. 4.

groups. Capillaries from various suppliers showing differences in surface concentrations might explain this assumption. On the other hand, the surface charges calculated with this equation are those at the boundary of the double layer. These charges are only proportional to those at the solid surface and the smaller number might be caused by the decrease in the electrical potential in the stagnant double layer. (The zeta potential is the electrical potential at the boundary between the stagnant and diffuse double layer [27].)

Fig. 1 also demonstrates that extremely high surface charges are required to accelerate further an already high EOF. As can be seen on doubling the surface charges from 0.6 to 1.2 μmol/m^2, the electroosmotic mobility increases only from $9.5 \cdot 10^{-4}$ to $10 \cdot 10^{-4}$ cm^2/N$\cdot$s. This is usually achieved with uncoated capillaries if the pH of the buffer is increased from 7 to 9.5 (compare Fig. 6).

More important for surface characterization, especially for modified capillary surfaces, is the opposite end of this curve at low surface charges. Even an extremely low concentration of surface charges (30 nmol/m^2) results in a relatively high electroosmotic mobility of 10^{-4} cm^2/V$\cdot$s. This means that to suppress the EOF totally, very good coverage of the quartz surface or high electroneutrality at the surface has to be achieved.

The possibilities of this approach for capillary surface characterization is discussed in the following.

EXPERIMENTAL

Reagents and materials

Fused-silica capillary tubes were purchased from Microquarz (a subsidiary of Siemens, Munich, Germany), Chrompack (Frankfurt, Germany), Polymicro (Laser 2000, Munich, Germany) and SGE (Weiterstadt, Germany).

Trichlorovinylsilane and trimethoxyvinylsilane were purchased from Chemische Werke Hüls (Marl, Germany) and *n*-butylamine, trimethylamine (gas), benzyl alcohol and all buffer substances from Fluka (Neu Ulm, Germany).

Methods

The real inner diameter was determined by weighing (Sartorius 4503 MP) an empty and a water-filled section (*ca.* 5 cm) of the corresponding type of capillary and calculating the difference.

Before use, all capillaries were rinsed with 1 M KOH solution (10 min), water (5 min), 1 M HCl (10 min) and water (5 min). Before silanization the capillaries were additionally rinsed with methanol (5 min) and subsequently dried overnight at 120°C under a gentle stream of argon.

Preparation of vinyl-modified capillaries

For all wall modifications only pretreated capillaries were used (see above).

Capillary V1. The capillary was filled with an emulsion of 3% (w/w) trimethoxyvinylsilane in water, containing 100 ppm of *n*-butylamine as a catalyst. After standing overnight at room temperature, the capillary was finally washed with methanol and water (20–30 min).

Capillary V2. The capillary was filled with a solution of 10% (w/w) trichlorovinylsilane in toluene and both ends were sealed. For reaction the capillary was kept in an oven at 120°C for 18 h. The solution was then driven out by a gentle stream of trimethylamine gas during 20 min at 120°C. After reaction the capillary was successively rinsed with toluene, dichloromethane, methanol and water.

Capillary V3. The capillary was filled with pure trichlorovinylsilane and both ends were sealed. For reaction the capillary was kept in an oven at 120°C for 18 h. After reaction the capillary was rinsed as for V2.

Apparatus

For EOF measurements a Beckman P/ACE system 2050 was used. Data acquisition was accomplished with Beckman Gold software (V 6.0) and an IBM PS 65 personal computer.

Benzyl alcohol was used as a neutral marker. Between the individual runs the capillary was washed for several minutes with methanol, water, 10 mM phosphate buffer (pH 9), water and the corresponding running buffer.

GC experiments were carried out with a Carlo Erba GC 6000 Vega Series instrument with flame

ionization detection. The length of the capillaries used for GC characterization was 1.5 m. The temperatures of the injection and detection system were set to 180°C. Nitrogen was used as the carrier gas with a linear velocity of 3.5 cm/s and the splitting ratio was higher than 1:20. To avoid overloading effects, very small amounts were injected (if possible the syringe was filled with the vapour of the sample).

RESULTS AND DISCUSSION

Comparison of uncoated quartz capillaries

General properties. So far quartz capillaries have not been produced exclusively for application in CE. Therefore, it is not surprising that materials from different suppliers vary in wall thickness, type and thickness of the protective polymeric coating, etc. In Table II the properties of four quartz capillaries available in Germany are summarized.

The greatest differences were found in the wall thickness of the capillaries, which varied between 49 and 129 μm. The optimum wall thickness is difficult to define. A thick wall is a good reservoir for generated Joule heat, and can serve for heat dissipation while working without additional cooling [29]. In this case the Polymicro capillary with a thickness of 130 μm certainly has some advantages. For thermostated systems this thick wall, on the other hand, prevents speedy heat exchange. In this case thin-walled capillaries would be more advantageous. The smallest wall diameter we found was 50 μm with the SGE

capillary. This capillary also had the thinnest polymeric coating, with a 10-μm film thickness. The thickest coating we found was 30 μm. The frequency of breakages did not correlate with the wall and protecting film thicknesses.

The effective inner diameter did not always correspond to the manufacturer's statement; in most instances the differences were within a range of 5% and only in one instance did the stated diameter of 75 μm differ widely from that measured. Because the inner diameter is identical with the optical path length, the detection sensitivity varies with the type of capillary used. From this point of view differences of 30% are intolerable. It is therefore recommended that the inner diameter of capillaries be determined experimentally by weighing the capillary empty and filled with water. The accuracy of these simple measurements is better than 1%. This procedure is recommended if longer pieces of capillaries are purchased, because we found that over a 10-m quartz capillary the inner diameter can vary by more than 5%.

Also important for detection sensitivity is the spectral transparency of the capillaries at low wavelengths. Fig. 2 demonstrates that at wavelengths below 220 nm the absorption of the quartz increases. Only the SGE material has a better transparency down to 210 nm, because of the smaller wall thickness. With the Polymicro capillary, which has the thickest wall, the absorbance of the wall increases continuously with decreasing wavelength, especially below 230 nm.

The influence of wall absorption on the detec-

TABLE II

MEASURED AND CALCULATED DIMENSIONS OF DIFFERENT TYPES OF FUSED-SILICA CAPILLARIES

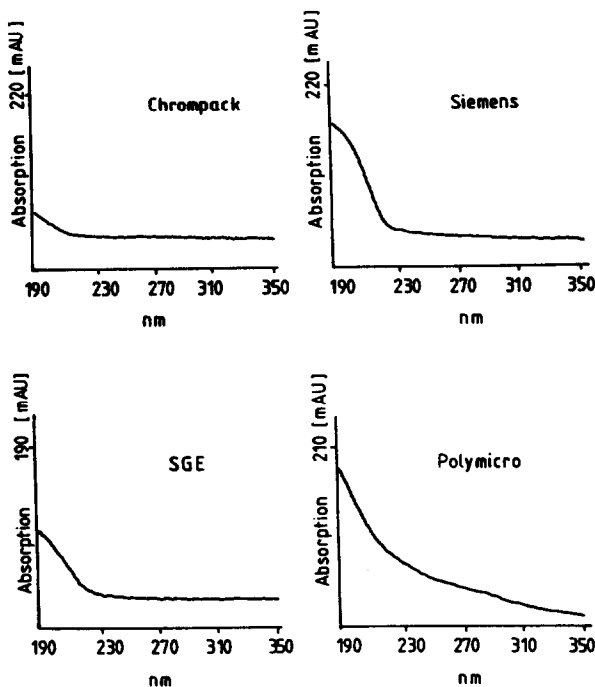| Parameter	Supplier			
	Microquarz	SGE	Chrompack	Polymicro
I.D. (quoted) (μm)	75	75	75	75
I.D. (actual) (μm)	71	74	53	74
O.D. (μm)	260	190	232	366
O.D. (no coating) (μm)	205	172	200	322
Coating thickness (μm)	28	9	16	17
Wall thickness (μm)	67	49	74	129

Fig. 2. UV spectra of different capillaries in the range 190–350 nm. Detector, GAT LDC 502 with CE cell (analogue of the Linear cell). All capillaries were filled with water.

Fig. 3. EOF *versus* pH curves for four different fused-silica capillaries. Conditions: $L = 40/47$ cm; buffer, 10 mM phosphate; neutral marker, benzyl alcohol; field, 425 V/m. ■ = SGE; □ = Microquarz; ◆ = Chrompack; ◇ = Polymicro.

tion sensitivity at 200 nm determined with sodium benzoate solution is negligible, however. The detection sensitivity is much more influenced by the inner diameter of the capillary and its position in the light beam and by focusing the beam through the liquid.

Electroosmotic flow and surface properties. The magnitude of the EOF is one of the most important factors in the optimization of CE separations. Therefore, the EOF was studied with the four different capillaries in the pH range 3–9. The resulting mobility measurements are shown in Fig. 3. Each capillary was treated identically by washing with sodium hydroxide and hydrochloric acid to achieve a reproducible and clean surface. In each instance the expected sigmoid shape could be observed [21]. At pH 3 the mobilities with all four capillaries are very similar. Only one (SGE) showed slightly higher mobilities than the others. The general shapes of the curves are identical, with an inflection point at pH 5–6. However, the differences in mobilities become significant at pH >5. With the
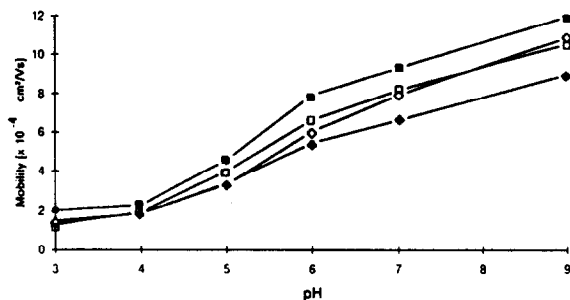
SGE capillary at pH 9 the highest mobility of $12 \cdot 10^{-4}$ cm/V·s was measured, compared with $8 \cdot 10^{-4}$ cm^2/V·s with the Chrompack capillary. The other two capillaries showed very similar mobility values of $1 \cdot 10^{-3}$ cm^2/V·s. This demonstrates that it is very problematic to transfer a separation from one type of capillary to another, because the mobilities may vary by more than 30% at higher pH values. In the standard CE mode (detection at the cathode) a high EOF is desirable to transport anions to the detector. The smaller the EOF at high pH, the longer the analysis time can become; it might even happen that fast anions are not transported to the detector and are lost for analysis.

As discussed in the Introduction, it is possible to determine the specific surface charges on the capillary wall from EOF measurement. In a first approximation one can assume that the inflection point around pH 5.5 of the curves shown in Fig. 3 corresponds to the pK_s values of the different types of quartz. Therefore, at pH 9 the surface silanols on the capillary wall should be totally dissociated. Consequently, it should be possible to determine from the magnitude of the EOF the concentration of surface silanols. As discussed already, the EOF is caused by differences in the zeta potential, which is active at the boundary of the stagnant and diffuse double layer. However, the charge density at this layer is a function of the surface silanols. The differences between this surface silanol concentration from EOF measurements and those calculated from crys-

talline quartz surfaces have already been dis-
cussed.

In Table III, the calculated surface concen-
trations of silanol groups are summarized.
Because there is no linear correlation between
mobility and surface charge density, the differ-
ences in silanol surface concentrations are higher
than the differences in mobilities. The smallest
value of 0.5 μmol/m^2 was calculated for the
Chrompack capillary, whereas for the SGE capil-
lary a value more than twice as high was calcu-
lated.

High silanol concentrations are certainly ad-
vantageous when chemical surface modification
has to be achieved. The stability and the effec-
tiveness of the binding increase with increasing
number of bonds of the coating to the surface.
On the other hand, the silanol groups are active
sites for cation exchange. Positively charged
solutes, especially proteins, interact with these
sites. This may cause a decrease in efficiency or a
total loss of samples. Capillaries with a lower
concentration of surface silanols may have ad-
vantages for these separations.

Characterization of coated capillaries

The effectiveness of coating procedures can
only be measured in CE via the variation of the
EOF or the efficiency variations of solutes which
may interact with the silanols as a function of
coating procedure. Non-polar coatings can be
additionally characterized by GC measurements
[19] via retention parameters. From the tempera-
ture dependence of retention parameters, Van 't
Hoff plots can be generated, the slopes of the

curves being proportional to the heat of sorption
of the solutes on the surface.

Coatings with linear acrylamide prepared by
transferring a method developed for the prepara-
tion of LC stationary phases [30] to CE capil-
laries have some advantages with respect of
stability and efficiency in protein separation [13].
The crucial step in the preparation of this type of
stationary phase is the reaction of surface
silanols with trichlorovinylsilane. In a second
step the introduced bonded vinyl groups are
copolymerized with acrylamide and other acrylic
acid derivatives. In LC it has been found that the
better the first reaction shields the silanols, the
better the stability of the stationary phase
becomes, and the less important is the contribu-
tion of silanols to solute retention. Therefore, a
method was developed to characterize via GC
measurements the CE capillaries modified with
vinylsilane in different ways. This step is of
paramount importance because with capillaries
modified with polar groups, such as linear
acrylamide, it is hardly possible to differentiate
between the influence of unshielded silanols and
that of the polar bonded groups.

The properties of capillaries reacted with vin-
ylsilanes in different modes were compared with
those of the untreated capillary. Capillary V1
was prepared with trimethoxyvinylsilane and *n*-
butylamine in aqueous suspension. Capillary V2
was obtained after treating the capillary with
trichlorovinylsilane in toluene and an additional
trimethylamine treatment. Capillary V3 was pre-
pared in the same way as capillary V2, but
without the introduction of a catalyst (for details,
see Experimental).

TABLE III

SPECIFIC SURFACE CHARGES FOR DIFFERENT FUSED-SILICA CAPILLARIES (CALCULATED FROM EOF AT
pH 9) (ACCORDING TO EQN. 4)

Supplier	μ_{eo} (cm^2/V·s $\times$ 10^{-4})	ζ (mV)	σ (μC/cm^2)	σ/F [a] (μmol/m^2)
Microquartz	10.59	134	7.93	0.82
SGE	12.00	152	11.90	1.17
Chrompack	9.02	114	5.33	0.55
Polymicro	10.91	138	8.58	0.91

[a] $F = 96\,500$ C/mol.

The gas chromatographic characterization was done with two different aspects. First, to measure the hydrophobic properties, the retention of n-heptane was studied. This molecule should show only the contribution of the bonded vinyl groups. Second, diethyl ether as a probe should demonstrate the polar interaction with the residual silanols.

In Fig. 4, the Van 't Hoff plot for heptane with the three different stationary phases is shown. The retention of heptane with the plain quartz capillary is very low, as it is with the vinyl-coated capillary prepared without a catalyst. The slope and hence the heat of sorption are identical and very small ($\Delta H = -13.5$ kJ/mol) in this case. The reaction of the silanes with silanols improves in the presence of a catalyst. As can be seen, for the other two capillaries not only are higher retention values obtained, but also the heat of sorption is much higher and relatively similar (V1, $\Delta H = -49.1$ kJ/mol; V2, $\Delta H = -55.9$ kJ/mol). If one assumes that with n-heptane only dispersive forces contribute to retention, it can be concluded that without a catalyst a silanization reaction hardly takes place. With the two other capillaries almost identical coatings must have been obtained with slightly higher coverage for V2.

The retention behaviour of diethyl ether and its temperature dependence, shown in Fig. 5, are much more difficult to explain. Diethyl ether interacts with silanol groups, and consequently the absolute retention on the uncoated capillary is high, as is the heat of sorption ($\Delta H = -53$ kJ/mol). Surprisingly low retention values were measured with capillary V3 prepared without a
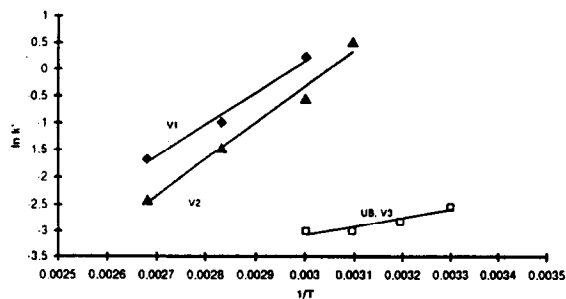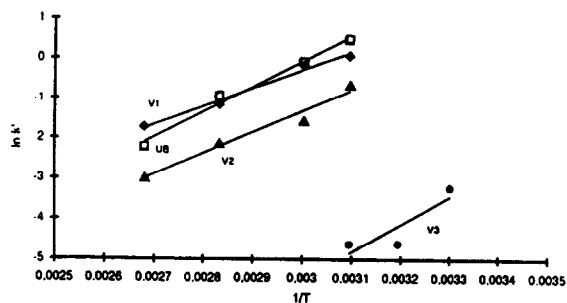
Fig. 5. Ln k' versus $1/T$ (Van 't Hoff plot) for diethyl ether with different modified and unmodified capillaries.

catalyst. However, the heat of sorption (slope) for diethyl ether is of the same order of magnitude ($\Delta H = -56$ kJ/mol) as with the untreated capillary. This indicates that the main contribution to retention is the interaction of diethyl ether with the silanol groups. Because of the small number of bonded groups, the dispersive interaction of diethyl ether is negligible. With the two other capillaries, where a higher coating was achieved, two mechanisms contribute to the retention of diethyl ether with the surface: dispersive forces and silanophilic interactions. Again, the heats of sorption determined for both capillaries are very similar, making it impossible to differentiate between the two mechanisms. The slightly higher value determined with capillary V2 ($\Delta H = -44.2$ kJ/mol) makes it feasible that dispersive interactions are the main contribution to retention of diethyl ether, and that here a slightly larger number of vinyl groups has been bonded to the surface.

In good correspondence with these findings are the conclusions that can be drawn from the EOF measurements as a function of pH shown in Fig. 6. By chemical modification the number of surface silanols and, consequently, the EOF are reduced. As can be seen in Fig. 6, the EOF with capillary V3 (slightly coated) shows a sigmodial shape identical with that for the uncoated capillary. At pH 9 the EOF is still 65% of that with the uncoated capillary. With the two other capillaries at pH 9 the EOF is only 30% of the initial value. Also, the shape of the curve is slightly different. Up to pH 6 the EOF is almost unaffected by pH. This can be explained by the finding from silica modification that mainly the
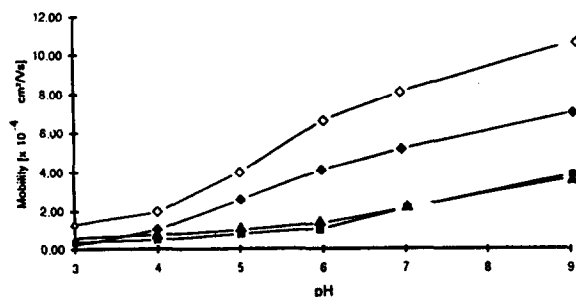
Fig. 4. Ln k' versus $1/T$ (Van 't Hoff plot) for heptane with different modified and unmodified capillaries.

Fig. 6. EOF *versus* pH curves for modified and unmodified capillaries. Conditions as in Fig. 3. ▲ = V1; ■ = V2; ◆ = V3; ◇ = uncoated.

highly acidic surface silanols react during silanization whereas the less acidic vicinal groups remain unreacted on the surface [31]. These groups are deprotonated at higher pH and only then contribute to the EOF.

There is a good correlation between the GC measurements and the dependence of EOF on pH. Consequently, it is possible to characterize at least non-polar coated capillaries. GC retention is dependent on the number of bonded groups. Further work is required in order to be able to obtain at least some insight into the total number of bonded groups. EOF measurements are correlated with the charge density at the double layer, which at least in part is influenced by the number of bonded groups on the surface. Both methods can therefore be used to obtain information on the surface properties of capillaries for CE.

ACKNOWLEDGEMENT

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