Electrophoresis in synthetic organic polymer capillaries: Variation of electroosmotic velocity and ζ potential with pH and solvent composition

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Electrophoresis in Synthetic Organic Polymer Capillaries: Variation of Electroosmotic Velocity and ζ Potential with pH and Solvent Composition

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The electroosmotic velocity occurring in capillaries made from polyfluorocarbon (PFC), polyethylene (PE) or poly(vinyl chloride) (PVC) was determined by the use of electrically neutral marker substances in dependence on the pH in aqueous solutions. The corresponding ζ potentials were calculated from the von Smoluchowsky equation. All curves, describing the variation of the electroosmotic velocity and the ζ potential, respectively, with pH exhibit the same shape, similar to a titration curve, with inflection points at pH 4.8 (PFC and PE) or 5.4 (PVC). With all materials the same value of the ζ potential of about −60 mV is reached at high pH (at an ion strength of 0.01 mol/L). It can be assumed that the surface charge is originating from the dissociation of carboxylic groups on the capillary surface. In contrast to fused silica, the adsorption of OH⁻ at high pH seems to play a neglectible role. The addition of organic solvents (ethanol, acetonitrile, or DMSO) to the aqueous buffer drastically reduces the electroosmotic velocity. The ζ potential, however, changes only to a minor extent in the concentration range of the organic solvent investigated (0-80% v/v). This result can be explained by the surface properties of the synthetic organic polymers.

INTRODUCTION

The electroosmotic flow is a well-known phenomenon in capillary electrophoresis, because most of the commercially available instruments are equipped with capillaries made from fused silica. This material has normally a negatively charged surface when brought into contact with buffer solution (see refs 1–9 and literature cited there). The source of this charge is 2-fold: surface silanol groups, which undergo protolysis, and OH⁻ ions adsorbed onto the surface.[9] The result is the formation of the electric double layer, and an electroosmotic flow occurs when an electric field is applied. This flow, directed toward the cathode in this case, enables the analysis of anions and cations by capillary zone electrophoresis in one run; it is also used in electrically driven separation methods like micellar electrokinetic chromatography or electrochromatography. On the other hand, the electroosmotic flow occurring in fused-silica capillaries is unfortunately very sensitive to changes of the surface and, therefore, shows often a low reproducibility.

Organic synthetic materials like polyflourocarbon (e.g. Teflon or related materials) have been used for about 20 years or longer in isotachophoretic instrumentation. These materials exhibit also a negative ζ potential,[1,3,10–13] but the electroosmotic flow can easily be supressed and controlled using additives like cellulose derivatives (cf. e.g. ref 10), which was a prerequisite for isotachophoresis in closed systems.

The formation of an electric double layer between the surface of an organic polymer and an electrolyte solution is, however, observed not only on polyfluorocarbon but also on many polymers like polystyrene, polyethylene, or polyurethane (see e.g. refs 14–20 and the literature cited there). It is assumed that this surface charge originates either from dissociative groups like carboxyl groups, incorporated in the capillary material, or from potential-determining ions adsorbed on the wall.

It was one goal of this contribution to investigate the electrokinetic properties of capillaries, made from materials with potential use in capillary electrophoresis, namely polyethylene and poly(vinyl chloride), and to compare the results with those observed from the commonly used flourocarbon material. These three materials are mechanically and chemically stable (PVC with some limitations) and are transparent for visible and near-UV light, which allows the on-column optical detection when used for capillary electrophoresis.[10]

Organic solvents are used as constituents of the electrolyte buffers for several reasons, e.g. to enhance the solubility of the analytes, to influence the mobilities of ions, to change the pK values of the sample components, to influence the electroosmotic flow, or to adjust the selectivity of the electrically driven chromatographic system. Reijenga et al. studied the influence of methanol on the ζ potential of Teflon capillaries by streaming potential measurements.[1] We investigated recently the effect of a series of organic solvents on the electrokinetic properties of fused silica.[9] In continuation of this work, the influence of ethanol, acetonitrile, and dimethyl sulfoxide on the electroosmotic mobility and on the ζ potential in capillaries made from the synthetic organic polymers is the subject of this paper.

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EXPERIMENTAL SECTION

Chemicals and Apparatus. The following chemicals were used to prepare the buffer solutions: sodium hydroxyde, boric acid (both analytical grade), orthophosphoric acid (85%), formic acid (98–100%) (all analytical grade, E. Merck, Darmstadt, Germany); betaine (anhydrous), DL-alanine (puriss) (both Fluka, Buchs, Switzerland); (cyclohexylamino)propanesulfonic acid (CAPS, Serva, Heidelberg, Germany).

The buffer solutions consisted of betaine (0.01 mol/L; pH range > 7.3) or CAPS (0.01 mol/L; pH range < 7.3), zwitterionic compounds at these pH values, which served as a background electrolyte in order to establish a relatively constant ionic strength (about 0.01 mol/L) over the entire pH range and to ensure only a low electric current in order to avoid excessive Joules heating. The pH of these buffer solutions was established by phosporic acid (0.001 mol/L; pH < 7.3) or boric acid (0.001 mol/L; pH > 7.3), adjusted with sodium hydroxide solution.

The organic solvents were dimethyl sulfoxide, ethanol, or acetonitrile (all analytical grade, E. Merck). Water was doubly distilled from a quartz apparatus.

The fluorescence-active neutral markers were 7-hydroxy-coumarin (umbelliferon, Fluka, in the acidic pH range up to 5.8), riboflavin (Serva, from pH 5.8 to 8), and rhodamine B (analytical grade, E. Merck, at pH higher than 8).

The following synthetic polymer capillaries were used for the measurements: polyfluorocarbon (a mixed perfluorinated polymer of ethene and propene; 200-μm i.d., 400-μm o.d., 24.3-cm length; obtained from the Technical University Eindhoven, Laboratory of Instrumental Analysis); polyethylene (150-μm i.d., 250-μm o.d., 24.3-cm length) and poly(vinyl chloride) (130-μm i.d.; 1.95-mm o.d., 23.0-cm total length) (both Thomafluid, Reichelt Chemietechnik, Heidelberg). All capillaries were clear and transparent to visible and near-UV light.

The apparatus for the measurement of the electroosmotic velocity was made in our laboratory and consisted mainly of the following parts: (1) the capillary, on which a centimeter scale was brought up using a fluorescing dye; (2) anodic and cathodic electrolyte vessels (Eppendorf vials of 1-mL content); (3) the electrodes, made from a platinum wire, connected with (4) the power supply unit (Model Alpha 2420, Brandenburg, Thornton Heath, U.K.).

The capillary was fixed in a housing, that shielded it from daylight. Into the housing a UV lamp (Blacklite-Blue, F6W/BLB, Sylvania) was mounted to cause the fluorescence of the neutral marker. This construction allowed the measurement of the electroosmotic velocity visually in a simple way with a stopwatch, without the aid of a detection instrument.

No special thermostating procedure was carried out: the capillary was kept at ambient temperature (23–24 °C).

Procedures. For the measurement of the electroosmotic velocity the electrode vessels and the capillary were filled with buffer solution. A solution of the marker substance in the same buffer was carefully inserted into the capillary at one end, either electroosmotically or (at low pH) hydrodynamically by applying different levels of the liquid in the vessels. In this way, an about 5-mm-long zone of the marker solution was inserted. The capillary was then dipped into the buffer electrolyte of the electrode vessels and care was taken that the liquid in both vessels was adjusted to the same level in order to avoid hydrodynamic flow.

For all measurements, the field strength was 22 630 V/m (voltage 5200–5500 V, depending on the length of the capillary). The current was below 20 μA in pure aqueous buffers with pH between 3.2 and 10, and below 50 μA at lower and higher pH; in the mixed solvents, much lower currents resulted. After the measurement of the migration velocity of the marker, the voltage was switched off, and the absence of a hydrodynamic flow was controlled by observing the marker zone for about 5 min. When no further migration was observed, it was assumed that no hydrodynamic flow occurred.

After each measurement, the capillary was carefully rinsed with several milliliters of buffer, and the capillary and both electrode vessels were filled with fresh buffer solutions.

RESULTS AND DISCUSSION

The dependence of the electroosmotic velocity, v, of the bulk liquid on the ζ potential, ζ, between the charged solid surface and the electrolyte solution is described by the von Smoluchowski equation:[21]

$$v = -\epsilon_0 \epsilon \zeta E / \eta \tag{1}$$

where ϵ_0 is the permittivity of vacuum, ϵ is the dielectric constant of the medium, η is its viscosity, and E is the strength of the electric field applied. In this relation it is assumed that the values for ϵ and η are equal for the electric double layer and for the bulk solution.

In analogy to the electrophoretic mobility of an ion, which is defined as its electrophoretic velocity at unit field strength, an electroosmotic mobility (of the bulk liquid) is defined by v/E. It can be seen, that this mobility depends (besides ϵ and η) only on the ζ potential. Thus, the ζ potentials established in the systems under investigation can be calculated directly from the measured electroosmotic mobilities, according to eq 1, using the values of the ratio ϵ/η for binary solvent mixtures published in a previous paper.[9]

It should be mentioned that the electroosmotic mobilities measured in a new capillary, that was not pretreated, was significantly higher, but these mobilities rapidly decreased during the first several runs (with rinsing in between the runs with 2 mL of 0.01 M NaOH and 2 mL of water). For PFC, e.g., the following sequence of the electroosmotic mobilities [given in 10^{-10} m^2/(V s)] was observed (at pH = 9) for the first seven measurements using a new capillary: 850, 762, 656, 552, 502, 491, 491. For PE, the analogue sequence was 739, 672, 615, 560, 505, 496, 496. PVC showed a similar behavior, starting with 790 [10^{-10} m^2/(V s)], but needed longer rinsing to get a constant value, namely 473 [10^{-10} m^2/(V s)].

For all polymers, however, the electroosmotic mobility established finally was stable over weeks or even over months of manipulation, remaining constant within the statistical error of the measurement, which was on the order of only a few percent. This error was mainly caused by temperature variations of the surrounding air (the measurements were carried out at ambient temperature between 23 and 24 °C without further thermostating). This good long-term reproducibility is in contrast with the behavior of fused silica, where it was difficult to get conditions sufficiently reproducible for such determinations.[9]

The results presented below were obtained with capillaries under stable conditions.

Polyfluorocarbon (PFC). *Aqueous Solutions.* The variation of the electroosmotic velocity in PFC capillaries with pH in pure aqueous solutions can be seen from Table I. At low pH the electroosmotic flow is directed toward the anode (possibly due to potential determining H$^+$ ions on the surface), but at pH values higher than about 2.5 this direction is reversed and the bulk liquid is transported to the cathode with a maximum velocity of 1.08×10^{-3} m/s under the given conditions (at an ion strength of 0.01 mol/L and a field strength of 22 630 V/m). The corresponding electroosmotic mobility, v/E, which was calculated by eq 1, follows the same trend (Figure 1) and exhibits a shape like a titration curve, with a maximum value of about 480×10^{-10} m^2/(V s). Compared to fused silica, the electroosmotic mobility is much lower, more than a factor of 2.[9]
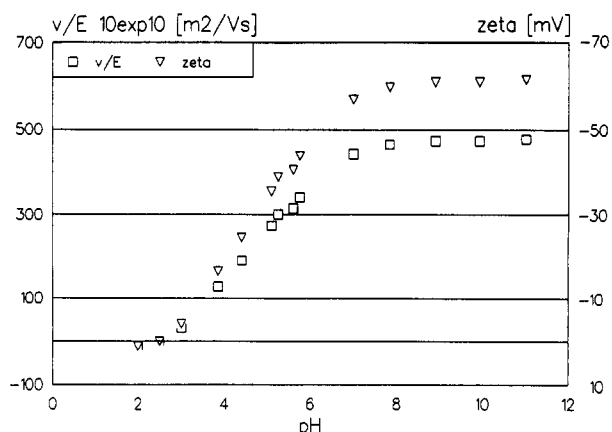
The corresponding dependence of the ζ potential on the pH shows a similar curve (Figure 1), with values from +1.3 mV at low pH to about –60 mV at pH values higher than 8. Again, a shape similar to a titration curve can be observed. The reason for this dependence can be attributed to the nature

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Table I. Variation of the Electroosmotic Velocity, v, with pH in Aqueous Solution in Capillaries of Different Materials[a]

| | $10^3 v$ (m/s) | | | | $10^3 v$ (m/s) | | |
pH	PFC	PE	PVC	pH	PFC	PE	PVC
2.0	−0.022	−0.022		5.8			0.61
2.5	0	0	−0.145	6.0		0.82	
3.0	0.07	0.07		6.2			0.64
3.1			−0.12	7.0	1.0		0.85
3.85	0.29			7.1		1.0	
3.9		0.29		7.83	1.05		
4.4	0.43			8.0			1.14
4.9		0.55		8.9	1.07		
5.0			0.32	9.0		1.11	1.14
5.1	0.62			9.93	1.07		
5.25	0.68			10.0		1.11	1.14
5.6	0.71			11.0	1.08		
5.75	0.77						

[a] Positive sign: flow toward the cathode. Negative sign: flow toward the anode. $E = 22.63$ kV/m.

Table II. Variation of the Electroosmotic Velocity, v, with Content of Organic Solvent at High pH[a]

| | $10^3 v$ (m/s) | | | | | | |
| % organic solvent (v/v) | ethanol | | acetonitrile | | DMSO | | |
	PFC	PE	PFC	PE	PFC	PE	PVC
0	1.05	1.11	1.09	1.11	1.04	1.05	1.14
20	0.53	0.55	0.96	0.95	0.71	0.67	0.70
40	0.33	0.33	0.88	0.87	0.40	0.38	0.41
60	0.21	0.20	0.85	0.84	0.22	0.22	0.23
80	0.16	0.16	0.85	0.84	0.19	0.20	0.20

[a] $E = 22.63$ kV/m.

Figure 2. Dependence of the electroosmotic mobility, v/E, on the composition of the mixed aqueous–organic buffer solvent in a polyfluorocarbon capillary. Values obtained at pH ≥ 10. For conditions see the Experimental Section.

Figure 1. Dependence of the electroosmotic mobility, v/E, and the ζ potential in a polyfluorocarbon capillary on the pH of the aqueous buffer electrolyte. For conditions see the Experimental Section.

of the negative charges on the surface of the capillary, carboxylate groups, originating from the production process of the PFC material. This assumption is supported by the fact that the inflection point of the curve, which corresponds to the pK_a value of the acidic functions on the surface, is 4.8, a value which is typical for aliphatic carboxylic acids. These results are in agreement with those published.[13–16,19,20]
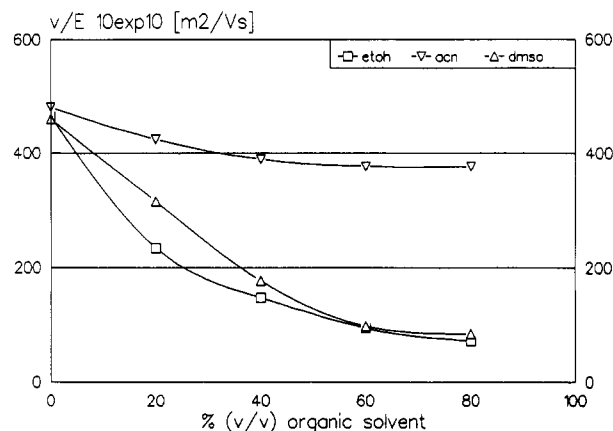
A similar dependence of the electroosmotic velocity or the ζ potential, respectively, on the pH of the buffer electrolyte was observed with capillaries made from fused silica or quartz. In these cases, also a curve resembling a titration curve was obtained. An overlooked but significant difference must be pointed out, however, when these materials are compared: the curve describing the dependence of the ζ potential on pH on PFC surfaces shows a plateau at high pH with constant values of the ζ potential. In this range the curve is parallel to the pH axis. This is not the case for silica surfaces, where the ζ potential increases with pH and does not reach a constant value at high pH.

This difference in the shapes of the curves can be attributed to the different chemical nature of the surfaces.[9] Fused silica is able to swell and to form gel layers and can easily incorporate OH⁻ ions by adsorption, which are well-known as being potential determining in such matrices. The extent of adsorption of OH⁻ is therefore dependent on the concentration of OH⁻ in the bulk liquid and increases with increasing pH. For this reason, no plateau parallel to the pH axis is formed by the ζ potential vs pH curve.

PFC, on the other hand, is a material that does not form such hydrophilic layers. It has, therefore, a very limited potential to adsorb ions like OH⁻ (whereby this effect cannot be excluded), with the result that the ζ potential does not increase further with increasing pH in the range of fully dissociated acidic surface groups.

Effect of Organic Solvents. The influence of ethanol, acetonitrile, and DMSO, added in a percentage between 20 and 80% (v/v) to the buffer solution at high pH, on the electroosmotic velocity is shown in Table II. The measurements were carried out at (apparent) pH between 10 (0% organic solvent) and 12 (80% organic solvent), in order to ensure that the electroosmotic flow is not influenced by the change of the degree of dissociation of the acidic groups on the surface, as discussed above. It must be taken into account that generally the pK_a values (and in particular those of the dissociable surface groups) are usually increased by the addition of organic solvents. Therefore the results about the influence of organic solvents on the ζ potential are very difficult to interpret when obtained in critical pH regions of the buffers, e.g. between 5 and 7.[1]

From Table II and from Figure 2 it can be seen that the electroosmotic velocity and the electroosmotic mobility decrease steadily with the increasing content of organic additive. This effect is most pronounced with ethanol, leading to a reduction to about 50% of the values in pure aqueous solution at 20% (v/v) ethanol, and reaching only one-sixth of the original values in a mixture containing 80% (v/v) ethanol. Whereas DMSO shows a very similar effect, acetonitrile reduces the electroosmotic velocity and the electroosmotic mobility, respectively, to a much lower extent.

The ζ potential, calculated from the electroosmotic velocity, according to eq 1, by the use of the data for the dielectric constant and the viscosity coefficients of the mixed aqueous–organic solvents given in a previous paper[9] are presented in
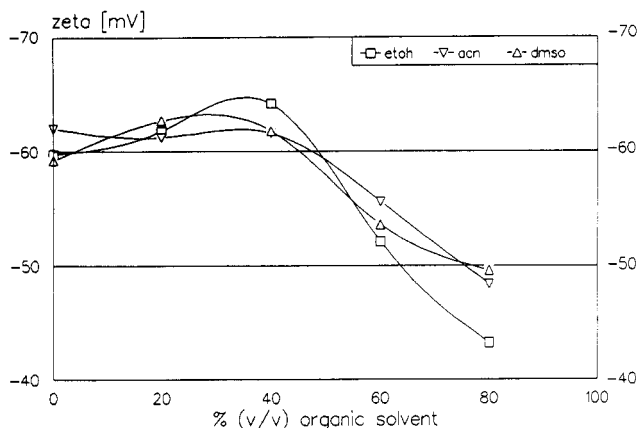
Figure 3. Dependence of the ζ potential on the composition the mixed aqueous–organic buffer solution in a polyfluorocarbon capillary. Values obtained at pH ≥ 10. For conditions see the Experimental Section.
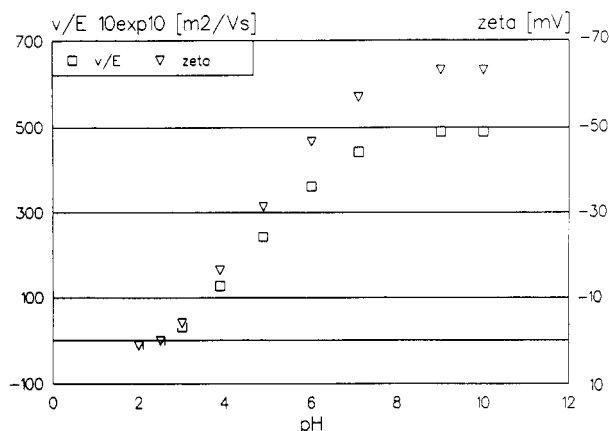

Figure 5. Dependence of the electroosmotic mobility, v/E, on the composition of the mixed aqueous–organic buffer solvent in a polyethylene capillary. See Figure 2 for conditions.

Figure 4. Dependence of the electroosmotic mobility, v/E, and the ζ potential in a polyethylene capillary on the pH of the aqueous buffer electrolyte. For details see the Experimental Section.

Figure 6. Dependence of the ζ potential on the composition of the mixed aqueous–organic buffer solvent in a polyethylene capillary. See Figure 3 for conditions.

Figure 3. In contrast to the electroosmotic mobility, the ζ potential is influenced only slightly by the organic additive, an effect which is totally different from that observed on silica surfaces. The values of the ζ potentials vary within only a few percent for all three additives up to 40% (v/v) organic solvent and decrease then to the same degree. The total change of the ζ potential is in the range of only 20–30%, whereas on quartz surfaces a drastic reduction to about one-third or one-fourth of the value in pure aqueous solution was observed.

This different behavior of PFC and quartz can be interpreted on the basis of the different mechanism of charge generation at high pH (were the acidic surface groups are fully dissociated), as discussed above. The predominant mechanism on quartz seems to be the adsorption of OH⁻ ions, supported by the special chemistry of the silica polymer. Organic solvents have a much lower ability to solvate ions (especially OH⁻ ions), compared to water, and destabilize this adsorption. On PFC surfaces, on the other hand, the adsorption of OH⁻ ions plays a neglectible role, compared to the dissociation of the carboxylic functions on the surface. This fact can be derived from the ζ potential vs pH curve in pure aqueous solutions, as discussed above. Therefore, the charge generation at high pH is much less dependent on the solvent.

The source of the slight variation of the ζ potential with the composition of the binary solvent mixture seems to be simply the small change in the ionic strengths of the buffers, originating from changes in the dielectric constants of the solvents.
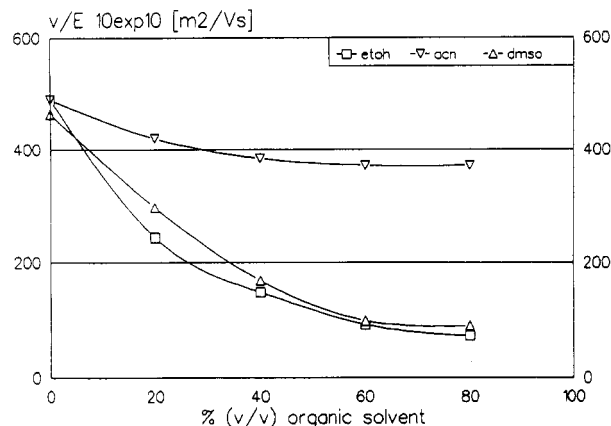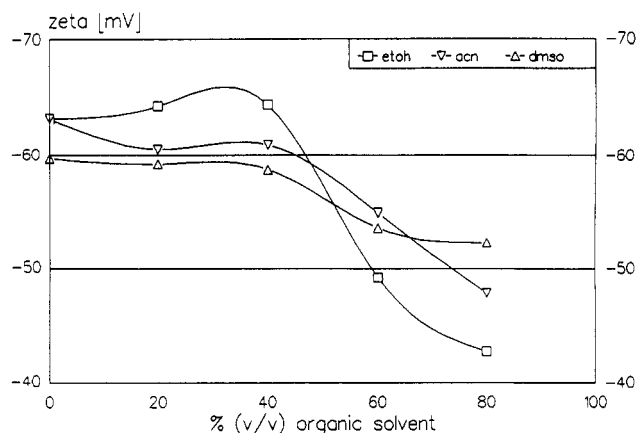
Polyethylene (PE). *Aqueous Solutions.* The influence of the pH of the buffer solution on the electroosmotic velocity in PE capillaries is shown in Table I. The measured values are similar to those observed in PFC capillaries. At low pH, the liquid streams are electroosmotically driven toward the anode, and the direction of the flow inverses at a pH of about 2.5. At a pH higher than about 8, a constant value of 1.11 × 10⁻³ m/s is reached, which is nearly the same as found for PFC surfaces. The small variations of the values are caused by the different temperature during the measurements (between 23 and 24 °C).

The dependence of the electroosmotic mobility and the ζ potential, respectively, on the pH in aqueous solutions is shown in Figure 4. Again curves with a shape like a titration curve are obtained, nearly identical with those from PFC, not only in shape but also with respect to the absolute values. This is an interesting result, because it means that not only the pK_a values (4.8) of the surface charge forming groups but also the charge density are about equal for both surfaces. Again it must be pointed out that the electrokinetic behavior of the PE surface differs in the same way as PFC from the silica surface for the reasons as discussed above.

Organic Solvents. Despite the different chemical natures of PE and PFC and despite the different types of production of the polymers, PE exhibits a nearly identical variation of the electroosmotic mobility with the composition of the mixed aqueous–organic solvents like PFC, as can be seen from Figures 2 and 5. Ethanol and DMSO influence the electroosmotic mobility strongly, and to the same extent, whereas acetonitrile has an only minor effect (see also Table II). The
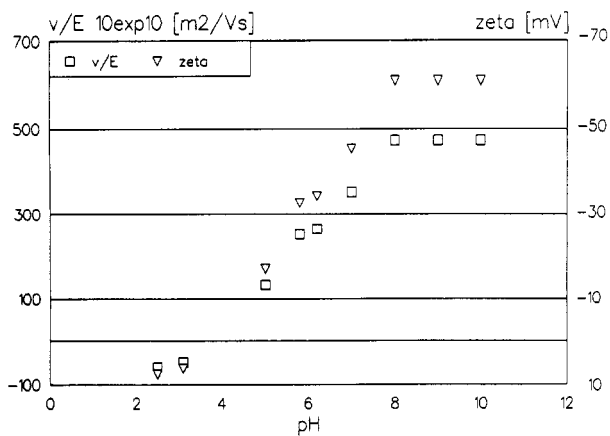
Figure 7. Dependence of the electroosmotic mobility, v/E, and the ζ potential in a poly(vinyl chloride) capillary on the pH of the aqueous buffer electrolyte. For conditions see the Experimental Section.
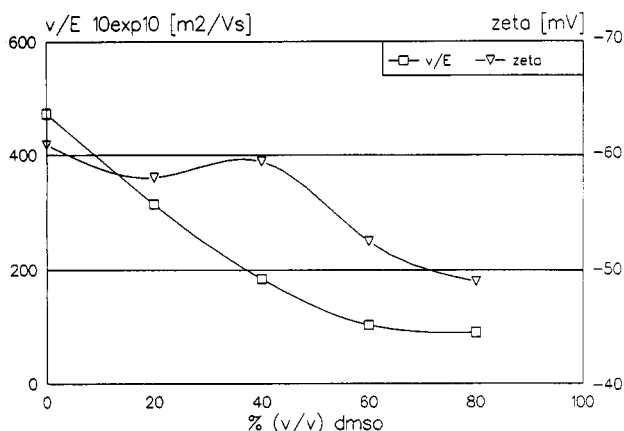

Figure 8. Dependence of the electroosmotic mobility, v/E, and the ζ potential on the DMSO content of the buffer solvent in a poly(vinyl chloride) capillary. See Figure 3 for conditions.

influence of organic additives on the ζ potential in a PE capillary is again considerably low, as demonstrated by Figure 6. The value of the ζ potential remains about constant at −60 mV up to 40% (v/v) organic solvent and decreases then slightly for all solvents by a factor of about 0.85 at 80 vol % of the organic solvent. Again it must be pointed out that this is a minor effect in comparison with the case of quartz surfaces.[9]

Poly(vinyl chloride) (PVC). *Aqueous Solutions.* The electroosmotic velocities at different pH values of the buffer are given in Table I. The values are similar to those obtained with the other capillaries, a fact which is also reflected by the values of the electroosmotic mobility, shown in Figure 7.

The curve of ζ potential vs pH (Figure 7) shows the same shape as those observed with the PFC and PE capillaries, but the inflection point, corresponding to the pK_a of the dissociable surface groups, lays at pH 5.4, 0.6 pH units higher. The maximum value of the ζ potential, obtained a high pH, is again the same as for the other polymers investigated.

Dimethyl Sulfoxide–Water Mixtures. The influence of ethanol or acetonitrile on the elektrokinetic properties of PVC was not investigated systematically, because it was found that the capillaries were not sufficiently resistant to the mixed aqueous–organic solvent in the long time range. The material, containing a plasticizer in a high amount, became hard and turbid in longer contact with the solvent. This effect was not observed for DMSO mixtures, and therefore the elektrokinetic investigations were limited to these solvents.

The variation of the electroosmotic velocity with solvent composition is given in Table II. For PVC compared to PFC and PE, nearly the same influence was found: the value of 1.14×10^{-3} m/s in the pure aqueous buffer is continuously reduced to 0.20×10^{-3} m/s at 80 vol % DMSO. The electroosmotic mobility is decreased by adding DMSO at a factor of about 5, as can be seen from Figure 8. As in the cases of PFC and PE, the ζ potential remains about constant up to 40 vol % DMSO and decreases slightly at a higher content of organic cosolvent, namely by only 15%, an effect which is also negligeable compared to the case with quartz.

CONCLUSIONS

The electrokinetic properties of capillaries of PFC, PE, and PVC are very similar. The dependence of the surface charge on the pH is caused by the protolysis of carboxylic groups located at the surface. The ζ potential is about half of that of fused silica under comparable conditions. In contrast to fused silica, it is influenced to only a very small extent by organic cosolvents like ethanol, acetonitrile, or DMSO, added as constituents of mixed aqueous–organic buffer solutions. It is, also in contrast to fused silica, highly reproducible even in the long time range.