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RECEIVED for review February 11, 1991. Accepted June 7, 1991. The support of the U.S. Environmental Protection Agency (EPA CK-815749-01-0) is acknowledged. The support provided by the Emil Aaltonen Foundation and Suomen Kulttuurirahasto is greatly appreciated (T.K.).

Electrophoresis in Fused-Silica Capillaries: The Influence of Organic Solvents on the Electroosmotic Velocity and the ζ Potential

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The influence of pH and solvent composition on the electroosmotic flow in fused-silica capillaries was studied. Binary mixtures of water and a protic (methanol, ethanol, 2-propanol) or an aprotic dipolar solvent (acetonitrile, acetone, dimethyl sulfoxide) were used for the buffer electrolyte. The dependence of the electroosmotic flow on the pH was determined in the pH range from 3 to 11 for pure aqueous solution and for solutions containing 50% (v/v) organic solvent. Adding organic solvents to the electrolyte, the inflection points of the resulting curves, corresponding to the pK values of the surface silanol groups, are shifted to higher values. At high pH, increasing the fraction of organic cosolvent generally decreases the electroosmotic velocity. ζ potentials were calculated from von Smoluchowski's equation using electroosmotic velocity data and values for the ratio of the viscosity coefficient and dielectric constant for binary mixtures, taken from own measurements and from the literature. With the exception of acetone-water mixtures, the ζ potentials obtained show a similar trend as the electroosmotic velocity: they decrease with increasing content of organic solvent. This trend is explained by changes of the dielectric properties of the electric double layer and of the charge generation on the fused-silica surface.

INTRODUCTION

The application of an electric field to a capillary filled with an electrolyte solution may generate an electroosmotic flow. For several types of electrophoretic techniques, this is advantageous. In capillary zone electrophoresis (CZE), e.g., it is possible to separate anionic and cationic species simultaneously in one run. In electrokinetic chromatography, use is made of electroosmosis instead of a pressure difference to transport the mobile phase because of the more favorable flow profile (1-5).

The addition of organic solvents to the electrolyte solution often extends the application range of electromigration methods. Aqueous-organic buffer electrolytes are used, for instance, to increase the solubility of analytes or to affect the acid-base properties of the sample components. In CZE, an increase in resolution is often achieved by lowering the elec-

troosmotic flow by using such buffer systems. In micellar electrokinetic capillary chromatography (MECC), the resolution of the analytes can be enhanced, when the selectivity is changed by adding organic solvents. In electrically driven liquid chromatography, organic solvents are often constituents of the eluent, too. In order to predict and control retention times, the electroosmotic flow rates have to be known in dependence on the concentration of the organic solvent.

Only very few data (6-8), but no systematic investigations on the electroosmotic velocities in organic or mixed aqueous-organic solvents, have been published. Thus, determinations of the electroosmotic velocity in different binary systems were performed and are presented in this paper. Six organic solvents, which are totally miscible with water and have favorable properties for use in separation techniques, are investigated. These three protic and three aprotic dipolar liquids have viscosities and dielectric constants varying over a wide range.

The electroosmotic velocity can be measured in different ways. One possibility lies in the measurement of the electroosmotic volume flow of the electrolyte solution with the help of a microbalance (9-11). By another method, the electroosmotic velocity is calculated in a very simple way from the migration time of an electrically neutral marker substance by using a capillary zone electrophoresis instrument.

To compare electrokinetic data and to get some insight into the processes taking place in the electric double layer, ζ potentials are calculated from the electroosmotic data by the use of viscosity coefficients and dielectric constants, taken from the literature and from our own measurements.

THEORY

Electric Double Layer. An electric double layer is created at the interface between a solid and a liquid phase, if a separation of charges is possible. In the case of a negatively charged solid surface, positive counterions will compensate the negative charge of the wall, thus forming a double layer. A part of the counterions will adsorb to the wall, giving rise to an immobilized compact layer. According to Grahame (12), the locus of the centers of the solvated ions is called the outer Helmholtz plane, whereas that of the contact-adsorbed anions, anions having stripped off their solvation sheath, is called the inner Helmholtz plane. The remaining counterions are distributed in a diffuse layer, their concentration approaching

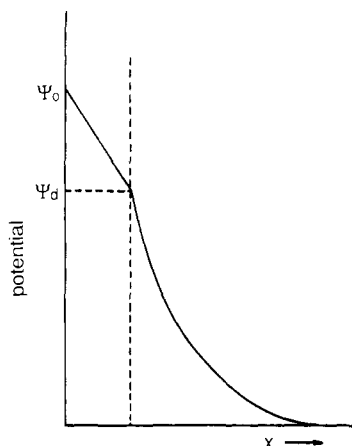


Figure 1. Variation of the potential in the electric double layer. ψ_0 , surface potential; ψ_d , potential at the beginning of the diffuse double layer; coincides with the ζ potential; x , distance from the wall.

the bulk value, as the distance from the wall increases to infinity (13). The potential drop is linear in the rigid layer, which is also called the Stern layer, but decreases exponentially within the diffuse layer as represented in Figure 1.

An expression for the potential distribution in the diffuse layer in the solution phase was first derived by Gouy (14) and Chapman (15), solving the Poisson-Boltzmann equation. It is given for a binary electrolyte with the valency $z^+ = -z^-$ by

$$\frac{d\psi}{dx} = \frac{2\kappa kT}{ze} \sinh \frac{ze\psi}{2kT} \quad (1)$$

where

$$\kappa = \left(\frac{2e^2 n^0 z^2}{\epsilon_0 \epsilon kT} \right)^{1/2} \quad (2)$$

ψ is the electric potential, x the distance from the wall or the outer Helmholtz plane, k the Boltzmann constant, T the absolute temperature, e the electric charge, n^0 the electrolyte concentration in the bulk solution, ϵ_0 the permittivity of vacuum, and ϵ the dielectric constant. In analogy to the Debye-Hückel theory, $1/\kappa$ is defined as the "thickness of the double layer" and is directly proportional to the square root of the ionic strength of the electrolyte solution.

While the electric double layer occurring at electrode surfaces, especially at mercury and AgI electrodes, is well understood, this is not the case for oxide surfaces like silica, because of the more complex surface properties.

The electric charge on oxide surfaces is mainly generated by two processes, surface dissociation and dissociative and nondissociative adsorption from solution, although these mechanisms are difficult to distinguish (16). Especially for the case of fused-silica surfaces, OH groups are not isolated but are in contact with each other via hydrogen bonding (17). They are formed by the adsorption of a first layer of water molecules onto the oxide surface. A second layer of adsorbed water molecules is hydrogen bonded to the first, whereby dissociative adsorption of H^+ or OH^- can take place.

The determination of the surface charge of silica by potentiometric titration yields very high values, much higher than would be expected from values for the potential of the diffuse double layer obtained from electrokinetic data (18). This leads to the conclusion that most of the surface charge is balanced by counterions adsorbed from the solution. Two different explanations have been proposed for this discrepancy:

The "porous surface" model assumes a porous (gel) layer of finite thickness (on the order of a few nanometers), in which all of the surface charge and also a large fraction of the counterions are located, resulting in a reduction of the ζ po-

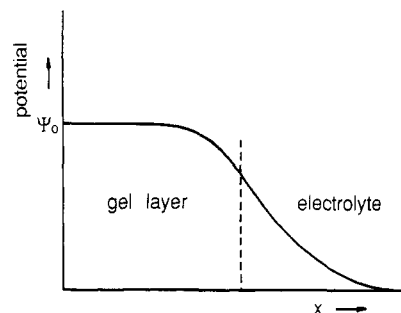


Figure 2. Anticipated potential distribution in a porous gel model of the oxide-solution interface (according to ref 16). ψ_0 , surface potential; x , distance from the solid oxide surface.

tential (19). The anticipated potential distribution is shown in Figure 2.

Tadros and Lyklema (20) gave evidence for the existence of a porous layer on silica. They observed a dependence of the surface charge density on the nature of the "indifferent" electrolyte, the term "indifferent" describing an electrolyte that contains no potential determining ions, namely H^+ and OH^- in the case of oxide surfaces. In addition, they did not observe an expected dependence of the surface charge density on the concentration of $(C_2H_5)_4NCl$, as was the case for alkali-metal ions. This led to the assumption that $(C_2H_5)_4N^+$, because of its size and hydrophobicity, could not penetrate inside the pores of the gel layer.

Churaev et al. (21) also stated the existence of a gel layer, which was, however, only observed after several days of contact of the fused quartz surface with the electrolyte solution.

A second approach to account for the discrepancy between the observed high surface charge and the low diffuse layer potentials is given by the "surface complex" model, where the best description is given by a triple-layer model (22, 23). This model incorporates the dissociation of surface silanol groups as well as the binding of normally indifferent ions in the Stern layer, which are regarded as forming complexes with the surface. The ζ potential is therefore reduced by the increased concentration of counterions in the immobilized layer.

§ Potential and Electroosmosis. When an electric field is applied to a capillary system, a part of the electric double layer is set into motion, giving rise to a flow of the liquid through the capillary. If the surface is negatively charged, as for the case of fused silica but also for perfluorinated polymers like Teflon (a material commonly used for capillary isotachopheresis (24, 25)), positive counterions in the diffuse double layer will move in the direction of the cathode, dragging the liquid along with them. On the other hand, solvent molecules, which are located close to the wall within the surface of shear, will not move under the influence of an electric field. This surface of shear is assumed to coincide with the outer Helmholtz plane (26, 27). The corresponding potential in this plane is called the ζ potential.

The velocity of the liquid rises from a value of zero at the surface of shear to a limiting value, v_{eo} , at an infinite distance from the wall, that is, the point at which the concentration of the positive counterions equals the bulk concentration.

The relation between the electroosmotic velocity, v_{eo} , and the ζ potential, as derived by von Smoluchowski (28), is given by

$$v_{eo} = -\frac{\epsilon_0 \epsilon \zeta}{\eta} E \quad (3)$$

where E is the applied electric field strength, ϵ is the dielectric constant of the medium, and η is the viscosity of the medium, assuming that ϵ and η have the same values in the double layer as in the bulk solution. The ζ potential can then be calculated

from values for the electroosmotic velocity and the ratio of the dielectric constant and the viscosity.

Limitations of this equation are caused by the fact that the values for the dielectric constant and the viscosity will change significantly under the influence of high electric field strengths. It was estimated that the ratio ϵ/η should increase by about 20% for a 0.01 M solution and a ζ potential of 75 mV (29), although this value was considered to be too high by other groups (30, 31).

EXPERIMENTAL SECTION

Chemicals. All chemicals and solvents used were of analytical grade (E. Merck, Darmstadt, FRG). Water was distilled twice from a quartz apparatus; the other solvents were used without further purification.

Buffer electrolytes were prepared in solvents consisting of different volume percents of the organic component. Because of the dependence of the electroosmotic flow on the ionic strength, an indifferent background electrolyte, having a 10-fold concentration compared to the buffering electrolyte, was added. Differences in ionic strength due to changes in the ionic concentration, when the pH is varied, are thus only of the order of about 10% or less. The electrolyte composition therefore used was for all measurements, 10^{-2} M KCl and 10^{-3} M phosphoric acid.

The pH of the electrolyte solution was adjusted by means of a glass electrode with a solution of KOH prepared in the respective solvent. The problem of using an all-aqueous glass-calomel electrode for the determination of the pH of a mixed aqueous-organic solution (where in fact the apparent pH, indicated as pH', is measured) was discussed elsewhere (32). For practical reasons, the pH', not the thermodynamic pH, was considered to be more suitable to describe the acidity of the buffer systems used for the determination of the electroosmotic flow.

Apparatus. For the determination of the electroosmotic velocity, a home-made capillary electrophoresis equipment was used, consisting of a fused silica capillary (96-cm total length, 43-cm length to the detector, 100- μ m i.d.) (SGE, Ringwood, Victoria, Australia), which was mounted in a fluorescence detector used in HPLC (Model F-1050, Merck-Hitachi). The high-voltage power supply unit (Tachophor 2020, LKB, Bromma, Sweden) was operated in the constant-voltage mode at 20 kV. Injection of the marker substance was carried out electrokinetically with 20 kV for 3 s. The detector signal was recorded by an integrator (Model D-2500, Merck-Hitachi).

The viscosity coefficients were determined with an Ubbelohde viscosimeter and a pycnometer, thermostated at 25.0 °C.

The dielectric constants were measured with a Type DK 03 instrument (WTW, Weilheim, FRG), thermostated at 25.0 °C.

Measurement of the Electroosmotic Velocity. Electroosmotic velocities were calculated from the migration times of the following neutral fluorescence active marker substances: umbelliferone (at pH values lower than 6), riboflavin (between pH 6 and 8), and 4-nitroaniline (at higher pH than 8). They were dissolved in the corresponding buffer electrolyte in a concentration of 0.1–1 mg/mL.

Measurements of the electroosmotic velocity were carried out at a field strength of 208 V/cm at ambient temperature of 25 °C, without further thermostating the capillary. Due to generation of Joule's heat, the temperature inside the capillary can be higher, but this effect is assumed to be less than 3 deg, because the working current was below 40 μ A in all cases (5).

RESULTS AND DISCUSSION

Reproducibility of the Electroosmotic Velocity. When a fresh fused quartz capillary is brought in long time contact with an electrolyte solution, different processes like gel layer formation, ion adsorption, or ion exchange may change the ζ potential and therefore the electroosmotic velocity with time. Thus, the reproducibility of the electroosmotic velocity within a single buffer system has to be improved before measurements obtained in electrolyte systems of different pH or solvent composition can be interpreted.

As an example for the changes in the electroosmotic flow, the migration times for a neutral marker are shown in Figure

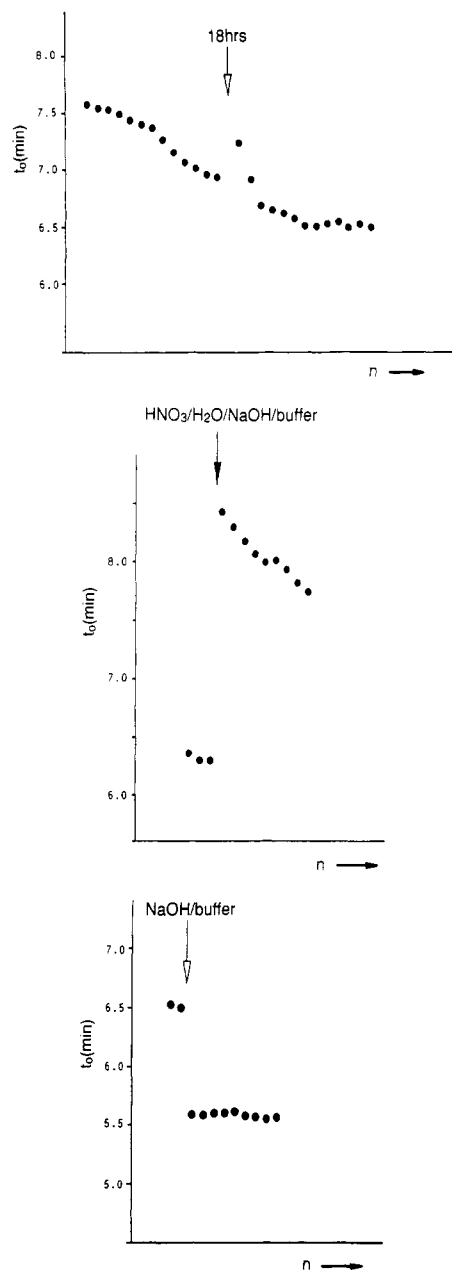


Figure 3. Reproducibility of the migration time of a neutral marker for consecutive injections. (a, top) Migration times in a fresh capillary without any pretreatment; the arrow indicates an overnight break. Average time between injections: 10 min. (b, middle) Migration times after rinsing steps with the specified solutions and water, respectively, as indicated by an arrow. (c, bottom) Migration times after rinsing steps with sodium hydroxide solution and buffer, as indicated by an arrow. t_0 , migration time of the neutral marker; n , number of consecutive measurements. For details, see text.

3 for consecutive measurements carried out in a fresh fused-silica capillary without any rinsing steps in between the runs. It can be seen from Figure 3a that the migration time is decreasing steadily, corresponding to an increase of the electroosmotic velocity. Rinsing the capillary with a solution containing a relatively high concentration (0.5 mol/L) of the potential determining ion H^+ results in a decrease of the electroosmotic velocity (Figure 3b), although the capillary was conditioned before measurements by rinsing with water, sodium hydroxide, and buffer solution. It takes several sets of 10 runs to restore the initial value. Similar findings were reported by Lambert and Middleton (33). A rinsing step with a solution of OH^- in a concentration of 0.5 mol/L between the consecutive measurements shown in Figure 3c leads to an

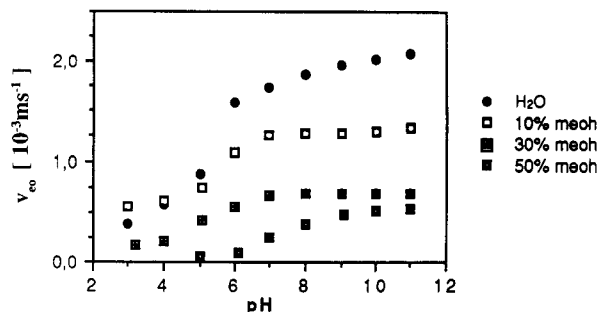


Figure 4. Dependence of the electroosmotic velocity, v_{eo} , on the pH (or pH') of the buffer electrolyte for pure aqueous and aqueous-methanolic solutions. Percentage given in v/v.

increase in the electroosmotic flow rate, whereby more stable conditions are obtained, as the following measurements show better reproducible migration times.

To prevent a decrease of the electroosmotic velocity observed during long time usage, possibly resulting from the formation of a gel layer, and to obtain a higher reproducibility within 1 day, the following procedure was found to be appropriate. A "fresh" surface was established every morning by rinsing the capillary first with 1 M HF for 30 s (corresponding to a volume of about 10 μ L); after a washing step with distilled water, the capillary was rinsed with KOH (1 mol/L) for 5 min (about 100 μ L) and then with the respective buffer electrolyte for another 5 min. In order to prevent the formation of a gel layer overnight, the capillary was dried by sucking air through it at the end of the day.

In between measurements, no rinsing steps with KOH were carried out. Because of the low buffer concentration, the electrolyte vessels were filled with new buffer after each run, as it was observed that the pH can change by some units when the same electrolyte solution was used for several consecutive measurements.

With this precaution and treatment of the capillary, a relative standard deviation of lower than 5% for the determination of the electroosmotic flow rate was obtained for long term usage, even with different capillaries.

pH Dependence of the Electroosmotic Flow in Mixed Solvents. The shape of the curve describing the dependence of the electroosmotic flow in a purely aqueous buffer system is already known from the literature (34) but was not discussed there in detail. Experimental data derived from measurements in the pH region between 3 and 11 are shown in Figure 4. Measurements were also carried out at pH 12, but a higher electric current due to an increased transport of OH^- generated a higher amount of Joule's heat, causing a decrease in viscosity. This resulted in too high experimental values for the electroosmotic flow, which were omitted for this reason.

The shape of a curve connecting the data points in Figure 4 resembles a titration curve; the inflection point of this curve may be interpreted as the pK value of the surface silanol groups. A pK of about 5.3 was found for the pure aqueous system. In contrast to a titration curve expected for such a weak acid, no plateau is reached when the pH is higher than the pK by 2 units, but the electroosmotic flow continues to increase slowly but steadily with pH. Also at a pH 2 units lower than the pK , the electroosmotic flow does not cease completely but maintains small values that are decreasing further with decreasing pH. This can probably be explained by the different mechanisms of surface charge generation, namely, surface dissociation on the one hand and ion adsorption on the other hand. Based on this model, the data in Figure 4 are interpreted as resulting from the superimposition of a titration curve (protolysis of the surface silanol groups) and an adsorption isotherm (depicting the adsorption of potential determining ions).

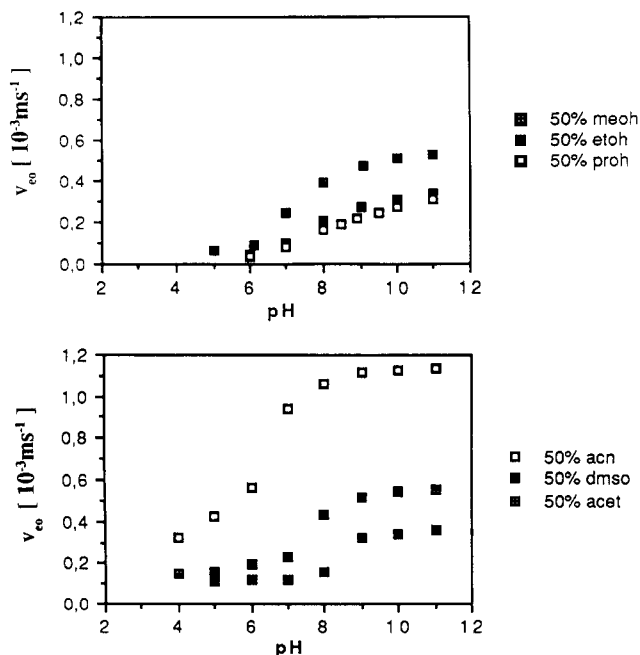


Figure 5. Dependence of the electroosmotic velocity, v_{eo} , on the pH (or pH') of the buffer electrolyte for solvent systems with a constant volume fraction of the organic solvent. Solvent code: meoh, methanol; etoh, ethanol; proh, 2-propanol; acn, acetonitrile; dmso, dimethyl sulfoxide; acet, acetone.

When organic solvents (three protic—methanol, ethanol, and 2-propanol—and three aprotic dipolar—acetonitrile, dimethyl sulfoxide, and acetone—were chosen) are constituents of the buffer electrolyte, two effects can be observed, as shown in Figures 4 and 5. The first effect is a decrease of the electroosmotic velocity with increasing concentration of the organic solvent, continuing also at high pH, where all of the surface silanol groups should be dissociated. This effect can be attributed to some extent to the increasing viscosity and/or decreasing dielectric constant and is discussed below.

The second effect is that the inflection point corresponding to the pK' of the silanol groups is shifted toward higher values when an increasing amount of organic solvent is added (see Figure 4 for methanol).

The influence of different organic solvents on the pK' is shown in Figure 5 for a constant percentage of 50% v/v. Dimethyl sulfoxide shows the largest effect, shifting the pK' of the silanol groups by more than 3 units, probably because of its poor ability to solvate anions. A less pronounced effect is observed when the buffer contains 50% v/v acetonitrile, as the pK' increases by only 1 unit, which is in agreement with expectations that acetonitrile acts as an almost inert compound in mixtures with water (35). These findings are in accordance with literature data (32, 36–41) on the influence of organic solvents on the pK value of weak acids.

Dependence of the Electroosmotic Flow on the Fraction of Organic Solvent. To study the influence of the addition of organic solvents on the electroosmotic flow, the pH' of the aqueous-organic buffer systems was chosen such that the dissociation of the silanol groups could be considered to be complete, and the electroosmotic velocity is almost independent of the pH'. Therefore, the pH' was adjusted to a value that was at least 3 units higher than the pK' of the silanol groups in the respective solvent. On the other hand, care was taken that the pH' was not so high that the electric driving current would rise drastically due to excessive transport of OH^- , which would cause increasing temperature effects as mentioned above. The pH' values chosen were thus between 9 and 12, increasing with higher amounts of organic solvent.

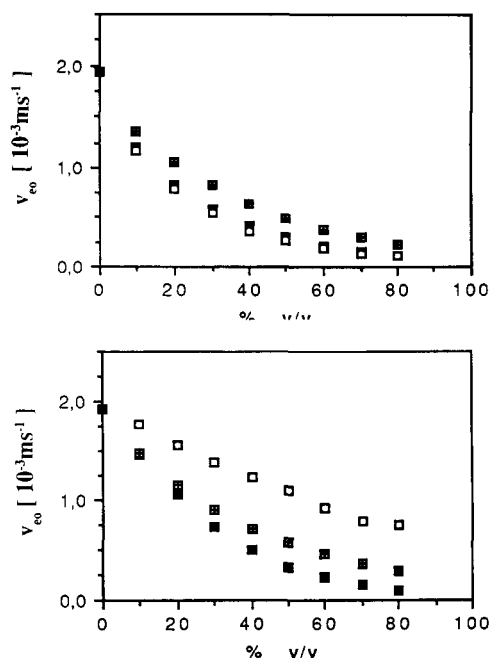


Figure 6. Variation of the electroosmotic velocity, v_{oo} , with solvent composition. Solvent code according to Figure 5.

The variation of the electroosmotic velocity with the content of the organic solvent is graphically represented in Figure 6. The overall trend is the same for all protic and aprotic solvents: a steady decrease in the electroosmotic velocity with an increasing fraction of the organic solvent. While for acetonitrile it falls off almost linearly, all the other solvents show a very steep decrease on addition of the first 30–40% organic liquid, reducing the electroosmotic velocity by a factor of about 3–4. A further addition of organic solvent leads to a continuing but slower decrease in the electroosmotic velocity. A fraction of 80% ethanol, 2-propanol, or dimethyl sulfoxide reduces the electroosmotic velocity by a factor of almost 20. Adding acetonitrile leads to a smaller decrease, which is one-third of the value obtained for water, at an acetonitrile concentration of 80% v/v. Determinations were not carried out at fractions of the organic solvent higher than 80% v/v, because then the buffer constituents were not sufficiently soluble.

Viscosity and Dielectric Constant of Mixed Solvents. In order to compare electrokinetic data in different aqueous-organic systems, having viscosities and dielectric constants varying over a wide range, ζ potentials are calculated from the electroosmotic velocity according to eq 3. For this purpose, the ratio of the dielectric constant and the viscosity, ϵ/η , has to be known for all binary systems consisting of water and an organic solvent.

In Figures 7 and 8, summarized data from measurements and from the literature (35, 42–45) of the viscosities and the dielectric constants are shown. A maximum in the viscosity occurs for all binary systems. Especially the dimethyl sulfoxide–water system shows a viscosity that is almost 4 times that of water at a volume ratio of water to dimethyl sulfoxide of 1:2 (corresponding to a molar ratio of 2:1). On the other hand, acetonitrile shows a very flat shape, displaying almost no increase in viscosity.

The dielectric constants show an almost linear decrease with increasing volume percent of organic solvent. Only dimethyl sulfoxide, having the highest dielectric constant of all organic solvents under investigation, shows a decrease in dielectric constant of only 10% in mixtures with water up to 60% v/v organic solvent.

The ratio ϵ/η in dependence of the percentage of organic solvent can be derived from the data from Figures 7 and 8;

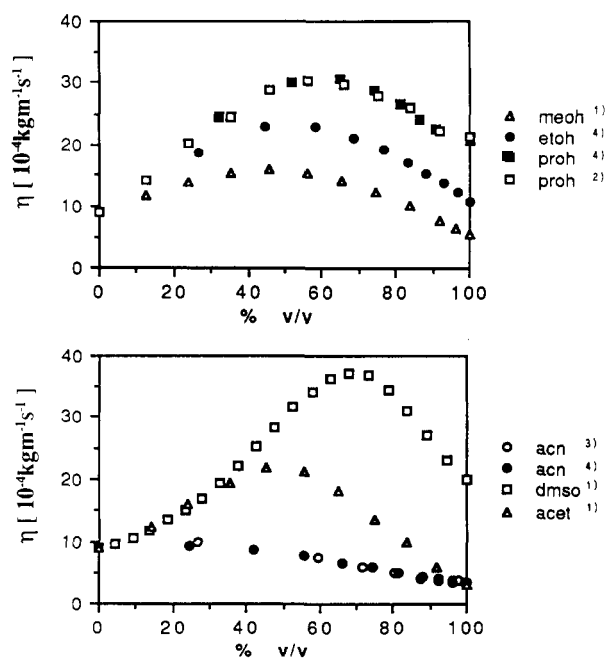


Figure 7. Dependence of the viscosity coefficient, η , on the fraction of organic solvent in binary systems with water for three protic and three aprotic solvents at 25 °C. (1) From ref 42; (2) from ref 43; (3) from ref 35; (4) own data. Solvent code according to Figure 5.

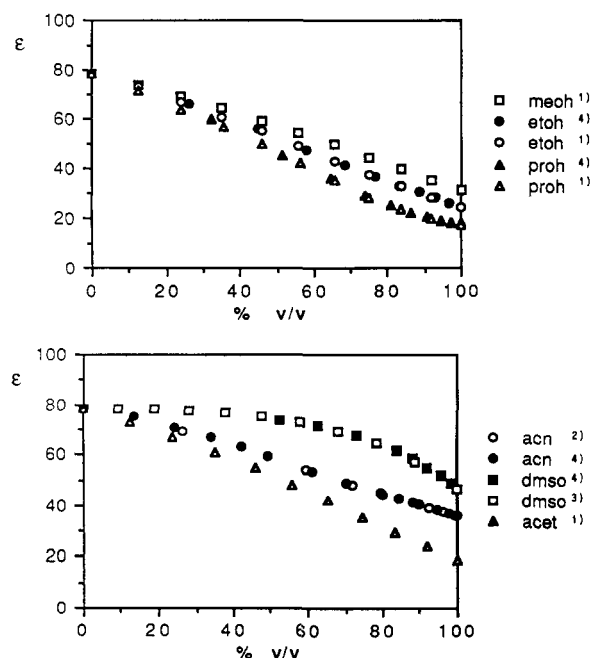


Figure 8. Dependence of the dielectric constant, ϵ , on the fraction of organic solvent in binary systems with water at 25 °C. (1) From ref 44; (2) from ref 35; (3) from ref 45; (4) own data. Solvent code according to Figure 5.

the resulting curves are shown in Figure 9. With the exception of acetonitrile, all of these curves show a similar steep decrease of the ratio ϵ/η with organic solvent fraction up to about 40% v/v. After passing through a minimum, the curves for acetone and methanol rise steeply again, while those for dimethyl sulfoxide, ethanol, and 2-propanol remain at low values. From these figures, it can be concluded that the variation of the electroosmotic velocity cannot be attributed solely to changes in the ratio ϵ/η .

Dependence of the ζ Potential on the pH and the Solvent Composition of the Buffer Electrolyte. Values for the ζ potential were calculated from the data for the electroosmotic velocity and the ratio ϵ/η using the relation

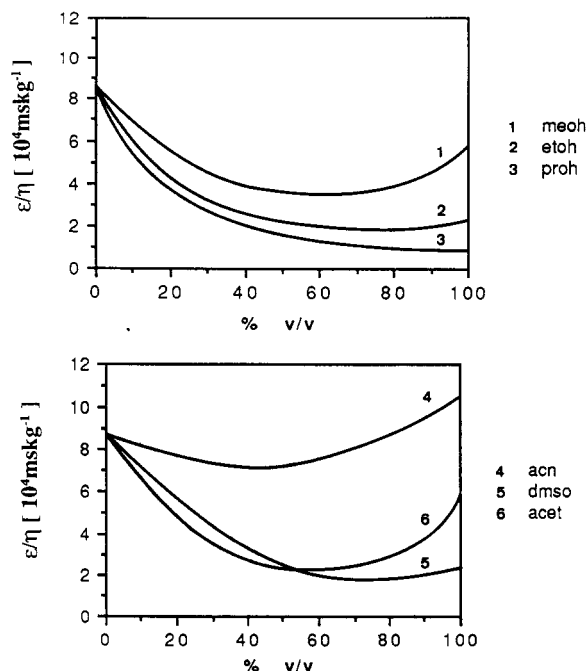


Figure 9. Variation of the ratio of the dielectric constant and the viscosity, ϵ/η , with solvent composition at 25 °C. Solvent code according to Figure 5.

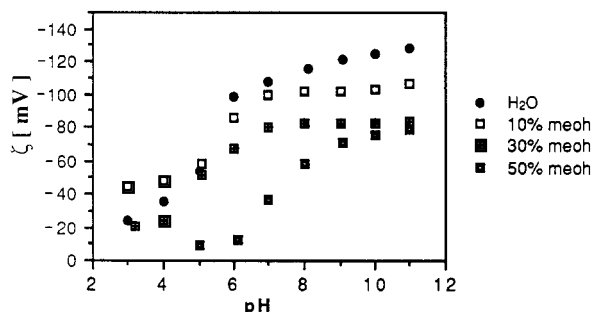


Figure 10. Dependence of the ζ potential on the pH (or pH') of the buffer electrolyte for water and different fractions of methanol. Percentage in v/v; solvent code according to Figure 5.

derived by von Smoluchowski (eq 3). The graphical representation of the dependence of the ζ potential on the pH of the buffer electrolyte is given in Figures 10 and 11. The ζ potential in the mixed aqueous-organic systems is significantly lower at high pH than in water for all solvent systems except 50% acetone, where the ζ potential reaches almost the same value at a pH' higher than 9 as in water. Below pH' 9, the ζ potential already falls off, mostly because the pK' is shifted to a value of about 7.5, compared to 5.3 in pure aqueous solution.

The results for the ζ potential in different aqueous-organic systems at high pH depending on the mole percentage of organic solvent are shown in Figure 12. An almost linear decrease of the ζ potential with increasing mole percentage of organic solvent can be observed for all mixtures, again with the exception of acetone, which shows a slight increase for concentrations up to 15 mol %. It then follows the overall trend, i.e., a decrease of the ζ potential on further addition of acetone.

Since the observed effects are rather large (the ζ potential is reduced by a factor of 2–4 at a solvent concentration of 50 mol %), they cannot be attributed to the limitations in applying the von Smoluchowski equation for calculating the ζ potential from electroosmotic velocity data. These limitations are due to deviations of the value of the ratio ϵ/η in the double layer from the bulk value. The introduction of a correction

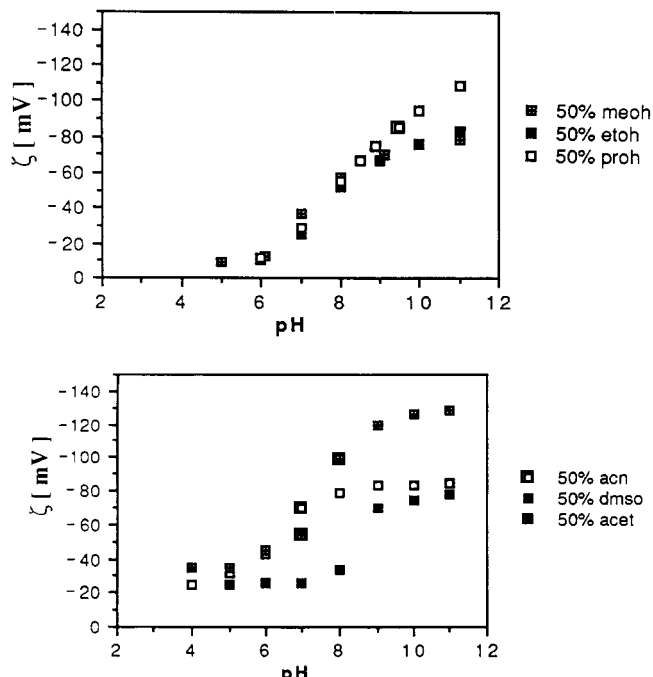


Figure 11. Dependence of the ζ potential on the pH' of the buffer electrolyte for solvent systems with constant percentage (v/v) of the organic solvent. Solvent code according to Figure 5.

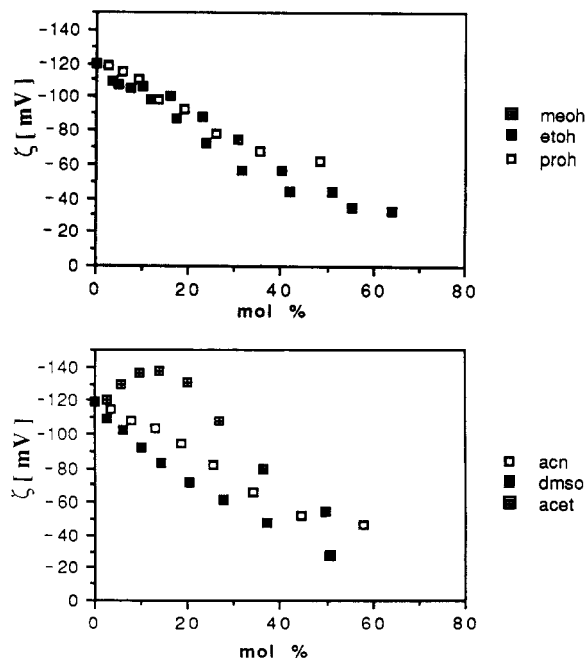


Figure 12. Variation of the ζ potential with solvent composition. Solvent code according to Figure 5.

factor would result in even higher potentials than calculated from the von Smoluchowski equation at high local field strengths (29). With decreasing potential also the deviations from this equation become smaller. Thus, corrections for the ratio ϵ/η would rather increase the overall trend that the ζ potential drops on addition of organic solvent.

Further, temperature effects, e.g., due to the changing driving current in the different solvent systems, will account for a maximum deviation of a few percent, as the ratio of ϵ/η is taken at a constant temperature of 25 °C. Also changes in ionic strength will show only a little influence on the data for the ζ potential, as already discussed above.

It can therefore be concluded that the addition of organic solvent actually reduces the ζ potential. Generally, either this

decrease can result from a steeper drop of the potential within the Stern layer (cf. Figure 1), compared to pure aqueous systems or it can be attributed to a reduction of the (negative) surface charge.

It can be assumed that the potential in the rigid layer will vary when organic solvent molecules are adsorbed to the surface of the capillary and are present in the solvation sheaths of adsorbed counterions. In this case, the dielectric properties of this layer are changed: the dielectric constant will be reduced (although it is not known exactly to what extent the dielectric constant in the compact layer decreases in the presence of organic solvent molecules). This effect will lead to a steeper potential drop and a lower value for the ζ potential.

This explanation, however, cannot account solely for the observed effects, because dimethyl sulfoxide-water mixtures, having the highest dielectric constants of all binary solvents investigated, show the steepest decrease of the ζ potential with increasing fraction of DMSO. The system acetone-water, on the other hand, having relatively low dielectric constants, displays the highest values of the ζ potential of all systems.

The second effect mentioned above results from the different mechanisms of surface charge generation. The adsorption of solvent molecules to the silica surface (46) can hinder the dissociative and nondissociative adsorption of potential determining OH^- ions. Organic solvent molecules will substitute water molecules adsorbed to the surface silanol groups, thus decreasing the number of adsorbed OH^- ions, as all of the organic solvents under investigation show a lower ability to stabilize anions via hydrogen bonding compared to water. In addition, the presence of organic solvent molecules in the Stern layer might also influence the adsorption of counterions depending on the different cation solvation properties of the organic constituents, therefore effecting the surface charge.

Both explanations—the variation of the dielectric constant and of the adsorption of ions in the compact layer—can account for the observed dependence of the ζ potential on the fraction of organic solvent.

CONCLUSIONS

It was found that in general the electroosmotic flow decreases steadily with increasing fraction of organic solvent. Calculated ζ potentials show a similar trend with the exception of the acetone-water system, which exhibits a slight increase on the addition of the first 40% v/v acetone. The variation of the pH of the buffer electrolyte leads to about the same dependence of the electroosmotic velocity as in water, resembling a kind of titration curve, whereby the inflection point (interpreted as the pK of the silanol groups) is shifted toward higher values with increasing content of organic solvent. As expected, the addition of dimethyl sulfoxide shows the largest effect, while acetonitrile has only little influence on the pK value.

From a practical point of view, the addition of dimethyl sulfoxide and ethanol leads to the most pronounced results,

when a reduction of the electroosmotic flow is desired, decreasing the electroosmotic flow by almost a factor of 20 at a fraction of 80% v/v organic solvent.

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RECEIVED for review December 18, 1990. Accepted May 29, 1991.