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Effect of Divalent Ions on Electroosmotic Flow in Microchannels

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Abstract

The electroosmotic flow (EOF) rate in fused silica microchannels is experimentally found to decrease when trace quantities of salts containing the divalent cations Ca^{2+} and Mg^{2+} are added to a constant ionic strength background electrolytic solution (BGE) flowing in a channel having negatively charged walls. Moreover, the observed effect is quantitatively different for the two ions Ca^{2+} and Mg^{2+} . Since electrostatic interactions are identical for ions of the same valence modeled as point charges, a description of the electric double layer (EDL) based on the Poisson-Boltzmann equation alone cannot account for these experimental observations. New experimental observations on electroosmotic flow in presence of Ca^{2+} and Mg^{2+} are reported in this work. A site binding model that accounts for the chemical interactions of the BGE ions with the silica surface is developed. The model predictions are in good agreement with the experimental observations on divalent cations as well as data from the literature on how properties such as pH and ionic strength affect electroosmotic flow rates for a BGE with monovalent cations.

Keywords

electroosmotic flow; electrical double layer; divalent ions; site binding model

1 Introduction

An electrolyte containing multivalent ions in contact with a silica (SiO_2)-containing substrate such as quartz, glass or fused silica is a situation commonly encountered in separation science (Kirby & Hasselbrink, 2004), biomedical (Zheng *et al.*, 2003), microfluidic (Sadr *et al.*, 2004) and geological (Revil *et al.*, 1999) applications. Previous research on the effect of divalent cations on a silica interface have indicated that even trace quantities of divalent cations can reduce the ζ -potential (Coreno & Sánchez, 2001; Pierre *et*

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al., 1990). In this work the effects of the divalent alkaline earth metal cations Ca^{2+} and Mg^{2+} on electroosmotic flow (EOF) are studied through a model of their electrostatic as well as chemical interactions ('site binding') with the silica surface. Mammen *et al.* (1997) appears to be the only study that uses a similar approach to model the effect of Ca^{2+} and Mg^{2+} on EOF.

Mammen *et al.* (1997) used a simple model of a silica surface groups (silanols) that either exist in a deprotonated state or undergo further chemical association with cations from the background electrolytic solution (BGE) solution to conclude that Ca^{2+} and Mg^{2+} associate with the silica surface to different degrees. The lower ζ -potentials observed for Ca^{2+} in comparison to Mg^{2+} was thought to be consistent with 'chemical intuition' based on the increase in polarizability (that leads to stronger Van der Waals interactions) and the decrease in hydrated ion radius in moving down Group II of the periodic table.

In this work, we utilize a more detailed and general picture of the silica-BGE interface than Mammen *et al.* (1997) that enables the model in this work to quantitatively account for the effect of other factors such as pH and ionic strength of the BGE on the ζ -potential and electroosmotic flow. Unlike Mammen *et al.* (1997), the model in this work accounts for both the substantial number of undissociated silanol groups on the silica surface and the adsorption of monovalent ions (Scales *et al.*, 1992; Revil *et al.*, 1999; Levine & Smith, 1971). The use of empirical 'co-operativity coefficients' between the surface-bound species (Mammen *et al.*, 1997) is avoided. The site binding model in the current work is combined with the Poisson-Boltzmann equation-based electrostatic picture of the diffuse part of the EDL, while in Mammen *et al.* (1997) it is proposed as a substitute for the Poisson-Boltzmann equation. Finally, a different technique (velocimetry) is adopted for electroosmotic flow measurements than the neutral marker time measurement in capillary electrophoresis used by Mammen *et al.* (1997).

An approach for calculating the distribution of ions in the EDL using the Poisson-Boltzmann equation for the electric potential is valid only in the diffuse part of the EDL (Hunter, 1981). The chemical interactions of interest in this work occur, instead in the Stern layer, which is immediately adjacent to the silica surface. The Stern layer is characterized by a lower dielectric constant than in the bulk; the electrolyte ions and their surrounding interfacial water molecules are hydrodynamically immobile and interact with the silica surface through electrostatic as well as non-electrostatic forces (Lyklema, 1991). The Stern layer adsorption of the divalent cations Ca^{2+} and Mg^{2+} and the differences between each divalent cation are studied in this work and their role in reducing the electroosmotic mobility is characterized experimentally and theoretically. A site binding model is developed by postulating a set of surface adsorption equilibria for the divalent ion and other BGE ions that can explain the reduction in electroosmotic mobility observed in the experiments.

In Section 2, we introduce the governing equations required to interpret EOF measurements. In Section 3, we develop a theoretical model of the effect of divalent cations on the ζ -potential and the experimental methods are described in Section 4. Theoretical results are presented in Section 5 and compared with the experimental data in Section 6. The conclusions are presented in Section 7.

2 Governing Equations of Electroosmotic Flow in Microchannels

To generate electroosmotic flow, an external electric field E_0 is applied to an aqueous electrolyte solution contained inside a straight microchannel of fused silica, glass or quartz with a length ($\sim \text{cm}$) several orders of magnitude larger than the cross-sectional dimensions ($\sim \mu\text{m}$). If ϕ is defined as the electric potential due to the EDL on the silica surface in absence of the electric field and u is the axial flow speed, it follows from Maxwell's

equations (Probstein, 1989) and the fully-developed form of the steady-state Navier-Stokes equations that:

$$\epsilon_e \nabla^2 \phi = -\rho_e \quad (1a)$$

$$\mu \nabla^2 u = \rho_e E_0 \quad (1b)$$

where ρ_e is the net volumetric charge density in the EDL. Here ϵ_e and μ are the electrical permittivity and the viscosity, of the electrolyte, respectively. The ζ -potential ζ is defined as the electric potential on the ‘shear plane’ dividing the immobile part (*i.e.* ‘Stern layer’) and the mobile part of the EDL. Equations (1a) and (1b) can be combined using this definition of the ζ -potential to obtain an expression for u as

$$u = -\frac{\epsilon_e E_0}{\mu} (\zeta - \phi) \quad (2)$$

Since $\phi \approx 0$ in the bulk of the electrolyte in the microchannel, the axial velocity is very nearly uniform in the bulk and decreases inside the EDL to a value of zero at the shear plane.

The characteristic thickness of the EDL as measured by the Debye length (Conlisk *et al.*, 2002) at the lowest ionic strength $I = 4.05 \text{ mM}$ used in the experiments reported in this work is 4.8 nm whereas the smallest channel dimension is $41 \text{ }\mu\text{m}$, nearly four orders of magnitude greater the Debye length. Therefore, Equation (2) can be averaged across the microchannel width, ignoring the contribution to the flow rate of the region inside the EDL. This gives the average velocity as

$$\bar{u} = \mu_{eo} E_0 = -\frac{\epsilon_e \zeta E_0}{\mu} \quad (3)$$

Evanescent wave-based or nano-particle-image-velocimetry (nPIV) is used in this work to measure $\bar{u}$ and calculate the electroosmotic mobility defined operationally as $\mu_{eo} = \bar{u}/E_0$. Use of this relation in Equation (4) gives

$$\mu_{eo} = -\frac{\epsilon_e \zeta}{\mu} \quad (4)$$

Equation (4) can be used to relate measured electroosmotic mobility value to the ζ -potential. The effect of Stern layer adsorption on the ζ -potential is modeled next.

3 Governing Equations of Stern Layer Adsorption

The electrolytic species of interest in this work that contribute to the surface charge of a silica surface are hydrogen ions, a monovalent cation M^+ , such as the sodium ion, a divalent cation N^{2+} , such as the calcium or magnesium ions, and an anion from the BGE, X^- . SH represents a surface-bound silanol group (a more concise notation instead of its ‘chemical formula’ SiOH) and S^- the corresponding silanolate anion ((SiO^-)) obtained on deprotonation of a silanol.

'Site binding models' (Kallay *et al.*, 2006; Scales *et al.*, 1992; Papirer, 2000; Levine & Smith, 1971) typically postulate the following reactions for the charge development on the silica-electrolyte interface in neutral to alkaline aqueous mediums:

The reaction represented by Equation (5b) can be viewed as an ion-exchange process leading to adsorption of M to form a neutral ionic silanolate species SM on the surface; this reaction is considered essential to realistically study the effect of so-called 'indifferent' cations such as sodium (Kirby & Hasselbrink, 2004; Scales *et al.*, 1992)

No consensus exists in the literature on the general features of the stoichiometry, mechanism and even the identity and location of the surface groups formed in case of a divalent cation N^{2+} adsorbing to a mineral oxide surfaces in general and silica in particular (Papirer, 2000; Criscenti & Sverjensky, 1999; Kallay *et al.*, 2006; Tadros & Lyklema, 1969). However, the following site binding reaction has been suggested (Criscenti & Sverjensky, 1999)

For many mineral oxide surfaces, the anion X^- originates from a salt in the BGE; for silica OH^- originating from interfacial water molecules has been considered a more appropriate choice for X^- (Criscenti & Sverjensky, 1999; Dove & Craven, 2005; Kallay *et al.*, 2006; Sverjensky, 2006). Two important features of this reaction are (a) the neutral species SNX does not affect the surface charge density to be neutralized by the diffuse layer. Further, in the case of silica, an alkaline medium ($\text{pH} > 7$) or an excess of $\text{X}^- \equiv \text{OH}^-$ favors the formation of SNOH. For the last reason, this reaction has been considered to play an important role at moderate to high pH values (Pierre *et al.*, 1990; Dove & Craven, 2005; Sverjensky, 2006).

As an alternative model for Stern Layer adsorption, a simple ion exchange process similar to Equation (5b) has also been considered appropriate for divalent cations (Düker *et al.*, 1995; Dove & Craven, 2005)

Unlike Equation (5b) and (6), adsorption *via* Equation (7) causes the divalent ion to introduce a positive charge in the non-diffuse part of the EDL. This type of adsorption can even result in the reversal in the polarity of the surface charge (Pierre *et al.*, 1990).

The law of mass action at equilibrium (Healy & White, 1978; Kallay *et al.*, 2006) can be used to calculate the equilibrium constants for these reactions in the following manner

$$K_{1=y} = \frac{[\text{H}^+][\text{S}^-]}{[\text{SH}]} \quad (8a)$$

$$K_M = \frac{\{H^+\} [SM]}{[SM] \{Na^+\}} \quad (8b)$$

$$K_{N1} = \frac{\{H^+\} [SNX]}{[SH] \{X^-\} \{N^{2+}\}} \quad (8c)$$

$$K_{N2} = y^{-1} \frac{\{H^+\} [SN^+]}{[SH] \{N^{2+}\}} \quad (8d)$$

where y is a shorthand for the electrostatic factor $\exp(-\zeta F/RT)$. This electrostatic factor arises because *electrochemical* equilibrium, and not chemical equilibrium, has to be considered at a charged interface (Hunter, 1981); for a thermodynamic derivation of Equation (8), see Healy & White (1978). Square brackets and curly brackets denote surface concentration in mol/m^2 and the activity (unitless) of a species, respectively. We note here that the use of ζ -potentials in y is an approximation; see the appendix for more details on the significance of ζ , y and K_i in Equation (8).

The total number density of surface silanols (N_s) is a constant

$$N_s = ([S^-] + [SH] + [SM] + [SNX] + [SN^+]) N_A \quad (9)$$

where $N_A = 6.02 \times 10^{23}$ is Avogadro's number. The values commonly ascribed to N_s range between $4 - 10 \times 10^{18}/\text{m}^2$, or in other words, 4 – 10 silanol groups per nm^2 of the silica surface (Iler, 1979; Papirer, 2000; Kirby & Hasselbrink, 2004).

The charge density neutralized by the diffuse layer is

$$\sigma = -([S^-] - [SN^+])F \quad (10)$$

Combining Equations (8), (9) and (10) gives

$$\sigma = -\frac{N_s F}{N_A} \frac{K_1 - K_{N2} \{N^{2+}\} y^2}{K_1 + y(\{H^+\} + K_M \{M^+\} + K_{N1} \{X^-\} \{N^{2+}\} + y K_{N2} \{N^{2+}\})} \quad (11)$$

where $\{H^+\} = 10^{-\text{pH}}$. In Section 5, when dealing with experimental data from the literature obtained in a BGE containing only monovalent ions (Wiese *et al.*, 1971), the surface charge density can be calculated from the theory of diffuse double layers when all ions in the solution are monovalent (Hunter, 1981)

$$\sigma = \frac{2\epsilon_e RT}{\lambda F} \sinh\left(\frac{\zeta F}{2RT}\right) \quad (12)$$

where λ is the Debye length defined by $\lambda = \sqrt{\epsilon_e RT / IF^2}$. Equation (12) is inserted in Equation (11) to derive a nonlinear equation for the ζ potential (or y) that can be solved numerically for ζ (or y) when all other parameters are specified. For theoretical predictions

that deal with multivalent ions in Section 5 and the experimental comparison in Section 6, a Debye-Hückel linearization of Equation (12) is used:

$$\sigma = \frac{\epsilon_e \zeta}{\lambda} \quad (13)$$

Equation (13) is accurate only for low ζ -potentials (Conlisk *et al.*, 2002); the surface charge densities calculated by Equation (12) and Equation (13) differ by 9.2% for the highest ζ -potential value recorded in the experiments reported in this work ($\zeta = -41$ mV). This ζ -potential value corresponds to a sodium tetraborate solution of $I = 10.8$ mM with no divalent cations so that Equation (12) is applicable. Equation (12) and Equation (13) are combined to study the effect of divalent ion concentration on ζ .

4 Experimental Methods

Nano-particle image velocimetry (nPIV) was used to measure the electroosmotic flow velocity within about 400 nm of the wall in fused-silica microchannels with a depth of 41 μm and a width of 312 μm or 469 μm (nominal dimensions) and an overall length of about 35 mm (Figure 1, right). The electrolyte solutions were driven from the anode towards the cathode by DC electric fields E ranging from 0.3 kV/m to 2.1 kV/m. In all cases, the region imaged (Figure 1, left) is well downstream of any bends to ensure fully-developed flow.

The fluids were seeded with fluorescent polystyrene spheres (Invitrogen FluoSpheres f-8888; absorption and emission maxima at 505 nm and 515 nm, respectively) of radius 50 nm (with a standard deviation of 6%) at a volume fraction of about 15 ppm. The fluorescent tracer particles were illuminated by evanescent waves generated using prism coupling of a 488 nm beam from an argon-ion laser (Coherent Innova 90) at maximum output power of 150 mW or less.

The penetration depth of the evanescent wave z_p , or the 1/e length-scale for the decay of the evanescent-wave intensity, was about 100 nm based on an angle of incidence of about 71.5°. The red-shifted fluorescence from the tracers is imaged by an inverted epifluorescent microscope (Leica DMIRE2) with a 63 $\times$ magnification, numerical aperture 0.7 objective (Leica PL Fluotar L) through a dichroic beamsplitter cube (Leica I3) and recorded by a CCD camera with on-chip multiplication gain (Photometrics Cascade 650) at a frame rate of 128 Hz with individual exposure times of 1 ms. Pairs of 100 $\times$ 653 pixels images (corresponding to a field of view of about 24 μm by 154 μm along the flow direction) with a temporal spacing $\Delta t = 7.8$ ms were processed using a FFT-based interrogation algorithm and a Gaussian surface-fitting peak-finding algorithm; relatively large interrogation windows of 180 $\times$ 60 pixels were used to minimize errors due to Brownian diffusion-induced particle mismatch within the image pair.

The velocities obtained here should correspond to bulk as well as the area averaged EOF velocity $\bar{u}$, since nPIV measures velocities within about $4z_p$ of the wall, or 400 nm, and the Debye length for a $I = 4.08$ mM electrolyte solution is about 4.8 nm; for $I = 10.8$ mM the Debye length is smaller. The nPIV velocities obtained using these processing were averaged over 4000 image pairs and plotted as a function of the driving electric field E . Linear regression of these data gave the electroosmotic mobility μ_{eo} ; the corresponding ζ -potential is obtained using Equation (4).

The working fluids used in this study are summarized in Table 1. Aqueous solutions of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) (decahydrate salt, ACS reagent grade, Acros Organics) with small amounts of calcium chloride (CaCl_2) (dihydrate salt, ACS reagent grade, EMD

Chemicals Inc.) or magnesium chloride (MgCl_2) (hexahydrate salt, ACS reagent grade, Fisher Scientific) and aqueous solutions of sodium chloride (NaCl) (ReagentPlus grade with 99.5% purity, Sigma Aldrich) with small amounts of CaCl_2 or MgCl_2 . Stock solutions were prepared with Nanopure water ($> 18.0 \Omega - \text{cm}$ resistivity, Ricca Chemical Company). The pH values for the $\text{Na}_2\text{B}_4\text{O}_7$ and NaCl solutions were measured to be 9.1 ± 0.1 and 5.7 ± 0.1 respectively. The NaCl solution is naturally buffered by atmospheric carbon dioxide (Butler, 1964).

5 Results

In this section and for the remainder of this work, N_s will be prescribed a value of 4.8 silanol groups per nm^2 (Raiteri *et al.*, 1996). The prefix p (as in pH) before any quantity is used to indicate the operator $-\log_{10}$, *e.g.* $pK_1 = -\log_{10}K_1$; the smaller the K_1 , the larger the corresponding pK_1 . The two equilibrium constants of divalent cation adsorption (K_{N1} via Equation (6) and K_{N2} via Equation (7)) will be denoted generically by K_N where the distinction is unimportant.

Figure 2 compares the site binding model predictions with the experimental data of Wiese *et al.* (1971) for ζ as a function of pH and salt concentration for aqueous solutions of the monovalent electrolyte potassium nitrate (KNO_3). This validation of the model illustrates the effects of parameters such as pH and salt concentration on the ζ -potential in monovalent electrolyte solutions and demonstrates that the model in the current work is more versatile than that of Mammen *et al.* (1997) as the latter cannot be used to study the effect of pH. The figure shows that a more alkaline solution (higher pH) gives a higher ζ -potential magnitudes, at least for a monovalent BGE. The slight uptrend in the zeta potential for the theoretical curves for 0.1 KNO_3 arises from an increase in ionic strength of the BGE that results when the pH of the solution is increased through addition of the base KOH, as in the experiments of Wiese *et al.* (1971). The ionic strength increase, which is particularly significant at low values of salt concentration and high pH values, provides better electrostatic screening to the surface charge resulting in a lower magnitude of ζ -potential. It is unclear why the same trend is not perceptible in the experimental data.

Equations (6) and (7) signify two distinct modes of divalent cation adsorption and Equation (11) is valid when the two adsorption modes coexist. To understand the applicability of Equations (6) and (7) with respect to the experimental measurements in the work, each of these two adsorption modes will be studied in isolation by setting the equilibrium constant of the other to zero. In Figures 3 and 4, the independent variable is the concentration of the divalent cation which can be either Ca^{2+} or Mg^{2+} depending on whether the salt CaCl_2 or MgCl_2 is present in the BGE whose primary constituent is a monovalent salt such as NaCl . The pH of the BGE can be increased and decreased by adding bases (such as NaOH) and acids (such as HCl), respectively, in presence of suitable buffers to produce acidic and alkaline solutions, respectively.

In Figure 3 the effect of the pH of the solution on the adsorption of divalent cations is studied; the two panes correspond to the two different modes of adsorption processes described by Equation (6) and Equation (7). Note that there is no firm agreement in the literature (Pierre *et al.*, 1990; Dove & Craven, 2005) on the dominant adsorption mechanism; Dove & Craven (2005) considers Equation (6) to be dominant at near neutral pH and Equation (7) to be dominant at alkaline pH values; Sverjensky (2006) uses Equation (7) at all pH.

The left pane of Figure 3 shows that the decrease in the ζ -potential due to adsorption of the divalent cations is greater in more alkaline solutions (at higher pH) if Equation (6) is the

dominant mode of adsorption. Figure 3(a) also shows that the ζ -potential eventually saturates and changes in the polarity of ζ -potential is impossible *via* Equation (6). The right pane of Figure 3 is based on Equation (7) as the only mode of adsorption. In this case, the adsorption process is much less sensitive to pH.

In either pane of Figure 4, the average velocity of the EOF is plotted against the concentration of divalent cation. As suggested by Mammen *et al.* (1997) as well our experimental observation (described in the next section), the higher sensitivity of the ζ -potential to Ca^{2+} can be attributed to its higher degree of association with the silica. Therefore, a higher value of the equilibrium constant K_N (lower pK_1) is used for Ca^{2+} than for Mg^{2+} regardless of the dominant mode of adsorption.

In the left pane of Figure 4 corresponding to the adsorption mode in Equation (6), the average flow velocity suffers a sharp drop followed by saturation; the drop as well as the flow rate at saturation is larger for Ca^{2+} . When adsorption takes place according to Equation (7) (right pane) the initial drop in average flow velocity is slower but the drop steepens with increasing divalent cation concentration. In fact, a reversal of flow direction is predicted. In either pane of Figure 4, the average velocity of EOF in a BGE containing Ca^{2+} is lower than that in a BGE containing Mg^{2+} .

6 Experimental Comparison

The experimental ζ -potential values and the theoretical predictions from the site binding model are compared in Figure 5. Good agreement is obtained between model predictions and the experimental data using the site binding model parameter values indicated on the figure and the experimentally measured pH values 9.1 and 5.7 for the $\text{Na}_2\text{B}_4\text{O}_7$ and NaCl solutions respectively.

The data for the $\text{Na}_2\text{B}_4\text{O}_7 - \text{CaCl}_2$ system is consistent with adsorption according to Equation (6) whereas the data for NaCl – MgCl_2 is consistent with adsorption according to Equation (7). The curves in Figure 5 with two data points ($\text{Na}_2\text{B}_4\text{O}_7 - \text{MgCl}_2$ and NaCl – CaCl_2) can of course be fitted by either model of adsorption; the choices shown in Figure 5 are consistent with adsorption according to Equation (6) at a high pH value ($\text{Na}_2\text{B}_4\text{O}_7$) and Equation (7) at a low pH value (NaCl) as supported by the literature (Pierre *et al.*, 1990; Dove & Craven, 2005) and Figure 3. This also facilitates a direct comparison between the effects of Ca^{2+} and Mg^{2+} by assigning a fixed adsorption mode to a given BGE.

For a given adsorption mechanism, Ca^{2+} required lower pK_N or higher K_N than Mg^{2+} . In the language of (Mammen *et al.*, 1997), this corresponds to a lower ‘dissociation constant’ of the site bound product species (e.g. SiOHCa and SiOCa^+) resulting from Equations (6) and (7).

A trial and error based curve-fitting procedure was adopted to obtain the equilibrium constants and the solid curves shown on Figure 5. Figure 6 makes a graphical assessment of the sensitivity of the calculated ζ -potentials to the equilibrium constant values chosen for divalent cation adsorption. Each pK value corresponding to divalent cation adsorption is changed by $\pm 5\%$ from their values in Figure 5 (i.e. the new values K_{new} for divalent cation adsorption are related to the corresponding old values K_{old} by $K_{\text{new}} = K_{\text{old}}^{1 \pm 0.05}$) to obtain the dashed curves, all other inputs to the model remaining fixed. The sensitivity of the ζ -potential in NaCl system ($K_{N1} = 0$) to K_{N2} increases with the divalent cation concentration; this effect is less significant for the $\text{Na}_2\text{B}_4\text{O}_7$ system because no new charged groups are created in response to the increase in divalent cation concentration when $K_{N2} = 0$ and also because the surface charge saturates at high divalent cation concentration values (*c.f.*

Equation (10) and Equation (11)). The highest percentage shift in ζ -potential at a concentration value populated by an experimental data point occurs at 0.04 mM Ca^{2+} , *i.e.* for the second data point from left of the $\text{Na}_2\text{B}_4\text{O}_7 - \text{CaCl}_2$ system. A 27% decrease and 29% increase in the magnitude of the ζ -potential results from a 60% increase and decrease of $K_{\text{NI}}^{\text{Ca}}$, respectively. In terms of absolute changes, the originally predicted ζ -potential of -12.4 mV (corresponding to an experimental ζ -potential is -10.4 mV) shifts to -9 mV and -16 mV , respectively, when the $K_{\text{NI}}^{\text{Ca}}$ value increases and decreases to $10^{4.305}$ and $10^{3.895}$ from the value $10^{4.1}$ shown in Figure 5, respectively. Although quantitatively significant deviations have appeared, the shape of the curves have the same qualitative features as the experimental data.

The sensitivity of ζ -potential values to other parameters can also be verified either graphically or by studying Equation (11) in combination with Equation (13). A change in K_1 affects the zeta potential at zero divalent cation concentration and in general, produces deviations that are several times (but not an order of magnitude) larger at low divalent cation concentration values than seen in Figure 6. Therefore a precise knowledge of K_1 is necessary for correct prediction of intercepts in a plot of ζ -potential with divalent cation concentration and similar plots with ionic strength and pH in monovalent BGE (Kirby & Hasselbrink, 2004; Revil *et al.*, 1999). The effect of K_M (monovalent cation adsorption) was found to be milder in terms of the dependence of ζ -potentials on the concentration of divalent cations than both K_N and K_1 ; this can be verified from Equation (11) and Table 1 by noting that K_M affects the surface charge density through a term which is nearly independent of divalent cation concentration.

7 Conclusions

A new site binding model was developed and found to be in good agreement with experimental measurements on electroosmotic flow in this work. A phenomenological approach based on equilibrium constants of site binding reactions at the silica surface is adopted and both electrostatic and chemical interactions of the ions with the surface are incorporated. The different adsorption behavior of the two divalent cations Ca^{2+} and Mg^{2+} can be explained by the stronger association of Ca^{2+} to the silica surface.

It is found that the results from the $\text{CaCl}_2 - \text{Na}_2\text{B}_4\text{O}_7$ system are best explained through Equation (6) while the results from the $\text{MgCl}_2 - \text{NaCl}$ system are well-explained by Equation (7). Unlike other models in the literature, the site binding model developed in this work can additionally be used to study the role of BGE properties and pH , both in the presence as well as the absence of divalent cations.

The intuitive reasons presented in Mammen *et al.* (1997) for the higher degree of association of calcium ions to the silica surface is consistent with the experimental ζ -potentials recorded at constant ionic strength NaCl solutions for Ca^{2+} and Mg^{2+} in this work, *viz.* the higher polarizability of Ca^{2+} leading to stronger Van der Waals interactions than Mg^{2+} as well as its smaller hydrated radius leading to closer distance of approach. Although the model here differs from that of Mammen *et al.* (1997), the higher degree of association of calcium still reflects as higher equilibrium constants K_N required for Ca^{2+} in NaCl or $\text{Na}_2\text{B}_4\text{O}_7$, *vs.* that for Mg^{2+} in NaCl .

The model developed in this work is essentially phenomenological because it requires empirically obtained equilibrium constants as inputs and more work is required to determine the exact physical properties of divalent cations that are responsible for the behavior observed in the experiments. Nevertheless, the experimental data for NaCl solution at $I = 10.8 \text{ mM}$ clearly suggest that the adsorption of Mg^{2+} is lower than that of Ca^{2+} .

While a much less common situation, the same effects considered here will be present when divalent anions are added to a solution flowing between positively charged walls.

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Appendix

The implications of the use of ζ -potential in defining the factor $y = \exp(-\zeta F/RT)$ used in Equation (8) are discussed below. The change in electric potential in moving from the shear plane (which is widely recognized to be coincident with the boundary of the diffuse layer (Levine & Smith, 1971)) to the plane of adsorption of the ion is assumed to be a constant and is lumped into the ‘equilibrium constant’ K_i (Healy & White, 1978; Revil *et al.*, 1999). Alternatives to this method are empirical treatments of the Stern layer as a capacitor (the ‘Basic Stern Model’ of Venema *et al.* (1996)) or a series of capacitors (the ‘triple layer model’ of Levine & Smith (1971)) but experimentally substantiated and theoretically well-founded values for these capacitances are yet to be determined (Sverjensky, 2001; Kirby & Hasselbrink, 2004; Levine & Smith, 1971). The use of ζ -potential as adopted in this work, avoids introducing these capacitances; thus minimizing the number of inputs to the model (Kirby & Hasselbrink, 2004) compared to other models of the silica interface in the literature (Venema *et al.*, 1996). On the other hand, since the actual change in electric potential between the plane of adsorption and the shear plane is not a constant but depends on factors such as the distance of the plane of adsorption from the surface, size and state of hydration of ions, and the surface charge itself (Sverjensky, 2001; Dove & Craven, 2005; Levine & Smith, 1971), a small but unavoidable sensitivity of the ‘equilibrium constants’ to the BGE conditions has to be accommodated to explain experimental observations. Obviously, this would not be the case for true thermodynamic constants (Healy & White, 1978).

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Figure 1.
The imaged region for npIV measurements (left) and the channel geometry.

Figure 2.

Effect of pH and concentration on the ζ -potential in an aqueous solution of KNO_3 : comparison of the site binding model with experimental data from (Wiese *et al.*, 1971). The site binding inputs were $pK_1 = 6.4, 6.25, 6.1$ and $pK_M = 2.2, 3.1, 3.5$ for 0.1, 1, 10 mM KNO_3 , respectively. Here M stands for K^+ .

Figure 3.

Theoretical prediction of the effect of the pH of the BGE on the ζ -potential vs. divalent cation concentration when adsorption follows (a) Equation (6) ($K_{N2} = 0$, $pK_{N1} = 3.5$) and (b) Equation (7) ($K_{N1} = 0$, $pK_{N2} = -5.5$). The same values of $I = 4.05$ mM, $pK_1 = 7.5$ and $pK_M = 3$ are used for either modes of adsorption.

Figure 4. Theoretical prediction of the average EOF velocity vs. divalent cation concentration curve of Ca^{2+} and Mg^{2+} when adsorption occurs according to Equation (6) (left pane) and Equation (7) (right pane). The same values of $I = 4.05\text{mM}$, $pK_1 = 7.5$ and $pK_M = 3$ are used for either modes of adsorption.

Figure 5. Effect of calcium and magnesium ions on the ζ -potential of sodium tetraborate: comparison of experimental and modeled values. The site binding model inputs are shown on the figure.

Figure 6.

The theoretically predicted zeta potential (dashed curves) when the pK value for divalent cation adsorption used in each of the solid curves of Figure 5 is changed by $\pm 5\%$ from the values shown in Figure 5, all other inputs to the model remaining unaltered from Figure 5. The solid curves and corresponding set of equilibrium constants are same as in Figure 5.

Table 1

Composition of divalent ion containing background electrolyte solutions used in the experiments. N^{2+} is Ca^{2+} or Mg^{2+} according as the BGE contains $CaCl_2$ or $MgCl_2$.

	Primary salt	Salt with divalent cation	$\frac{[N^{2+}]}{[M^{+}]} (\%)$	I(mM)
I	$Na_2B_4O_7$	-	0	4.05
II	$Na_2B_4O_7$	$CaCl_2$	1	4.05
III	$Na_2B_4O_7$	$CaCl_2$	5	4.05
IV	$Na_2B_4O_7$	$CaCl_2$	8	4.05
V	NaCl	-	0	10.8
VI	NaCl	$CaCl_2$	1	10.8
VII	NaCl	$MgCl_2$	0	10.8
VIII	NaCl	$MgCl_2$	1	10.8
IX	NaCl	$MgCl_2$	2	10.8
X	NaCl	$MgCl_2$	3	10.8