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Slow change in the electrical potential at glass and silica surfaces due to Na^+ sorption in the hydrated layer

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Abstract

Controlled Pore Glass (CPG) is a high- SiO_2 content, Vycor-type glass which resembles fused silica. In CPG–Oxine the ligand oxine is covalently bound to the CPG surface. The presence of SiO^- groups on the CPG generates a negative electrical potential at the surface (ψ_0) and also in the solution adjacent to the surface (ψ_x), where the immobilized oxine is to be found. The potential ψ_x influences the extent of complexation of Ca^{2+} (from solution) by oxine so that the bound oxine serves as a probe of electrical potential near the surface. When the solution pH is raised there is a relatively rapid ionization of SiOH groups to SiO^- . Then, slowly (i.e. tens of minutes), Na^+ from solution diffuses into the hydrated gel layer on CPG. This reduces the negative charge, making ψ_x less negative and, consequently, reduces the extent of complexation of Ca^{2+} by oxine. A linear relationship is predicted and experimentally observed between the logarithm of the sorbed Ca^{2+} concentration (mmol/g) and the potential ψ_x (V). The potential ψ_x is expected to correlate strongly with the zeta potential which controls the rate of electroosmotic flow at silicious surfaces.

1. Introduction

Silicious materials such as glass and fused silica possess a thin (e.g. tens of Å) hydrated layer when they are in contact with aqueous solutions. Depending on the solution pH, there is some ionization of the acidic SiOH groups to form SiO^- groups, both at the surface and in the hydrated layer [1–3]. The presence of these SiO^- groups generates a negative electrical potential at the surface (ψ_0) and also in the solution adjacent to the surface (ψ_x). These potentials influence sorption of solutes at the surface and

they are related to the electrokinetic zeta potential (ζ) which controls electroosmotic flow [4–6].

By measuring both the extent of deprotonation of the SiOH groups and the extent to which cations such as Na^+ are sorbed from solution, the total charge is known. However, the development of a quantitative expression to calculate the electrical potentials from a knowledge of the total charge requires the adoption of a detailed physicochemical model. The validity of the adopted model and of the resulting equations for calculating potentials must then be demonstrated experimentally. This is done by introducing a potential-sensitive “probe” whose behavior is a known function of potential. Then the observed behavior of the probe can be compared

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to that expected from the potentials calculated from the assumed model.

The present study is based upon earlier observations of the influence of pH, ionic strength and time on the complexation of Ca^{2+} ion by a ligand, when the ligand is covalently bound to the silicious surface of Controlled Pore Glass (CPG) [4,5]. In Controlled Pore Glass–Oxine (CPG–Oxine) the 5-phenylazo derivative of 8-hydroxyquinoline, which is bound to the surface of CPG [7,8], serves as a potential-sensitive probe since its ability to complex Ca^{2+} has a predictable dependence on the local electrical potential. Because only a very small fraction of the surface silanol groups in CPG–Oxine are derivatized with the oxine ligand, the surface of CPG–Oxine is much like that of CPG. Also, although the bound oxine groups have acid–base character, titration studies have demonstrated that most of the charge on CPG–Oxine is due to anionic silanolate groups from the CPG, and only a very small fraction is due to the ionized oxinate groups from the ligand [1].

The way in which the bound oxine ligand acts as a probe for the local electrical potential near the surface is as follows: the negative charge on the CPG creates a negative electrical potential which, via Boltzmann expressions, influences the activities of mobile cations and anions (e.g. H^+ , Ca^{2+} , Na^+ , OH^- , and ClO_4^-) in the solution immediately adjacent to the surface; that is, in the electrical double layer region [6,9]. These altered local solution activities, in turn, influence the equilibria in this region, wherein the immobilized oxine groups are located. In particular, the local pH (pH) in the vicinity of the oxine group is lower than the pH in bulk solution. This pH is what influences the degree of ionization of the immobilized oxine, $\bar{\alpha}_{\text{ox}}$. Also the local ionic activity of Ca^{2+} , \bar{a}_{Ca} , is higher than a_{Ca} in bulk solution. The local $\bar{\alpha}_{\text{ox}}$ and \bar{a}_{Ca} influence the extent to which Ca^{2+} is complexed by immobilized oxine. Using bound oxine as a probe, it has been found that most of the equilibrium properties related to the complexation of Ca^{2+} ion by the immobilized oxine ligand could be explained by a simple version of the “ionizable surface

group, site-binding model” [1,4]. This type of model is used widely in surface and colloid chemistry [6,9].

More recently, studies were undertaken to explain an anomalous aspect of the kinetics of Ca^{2+} sorption by CPG–Oxine [5]. The anomalous behavior was an “overshoot” of equilibrium during the loading of Ca^{2+} onto small columns of CPG–Oxine which had previously been washed with acid and water. The Ca^{2+} -loading curve, which is a plot of moles of Ca^{2+} sorbed versus time, rose to a maximum value in about 2 min and then decreased over the course of about 2 h to a final equilibrium plateau value. The following interpretation of this phenomenon was suggested [5]. The slow desorption of Ca^{2+} from its overshoot sorption value to its equilibrium value is caused by the sorption of Na^+ . The casual relationship between these two is not a stoichiometric one, such as ion exchange, but rather results from the effect that Na^+ -uptake into the hydrated layer has on the potential in the electrical double-layer region. Furthermore, it was suggested that the reason why the sorption of Na^+ is a slow process is because it involves diffusion of Na^+ into this “porous gel” hydrated layer, within which the diffusion coefficient of Na^+ is very small.

In the present paper a physicochemical model is developed to quantitatively explain the kinetic aspects of the cause-effect relationship between slow Na^+ sorption and electrical potential. The validity of this model is tested on CPG using covalently bound oxine as a probe of electrical potential. Since CPG is a high-silica content glass [10], it is likely that a similar slow sorption of alkali metal cations will occur on fused silica and other related materials that are of chromatographic and electrophoretic importance; and that this slow sorption will also be accompanied by a slow change in potential. Because CPG is porous, it possesses a high surface area–mass ratio, which permits accurate measurement of the amounts of sorbed species. In addition to the rate studies, as part of the work, the equilibrium sorption isotherm of Na^+ in the hydrated layer is characterized.

2. Experimental

2.1. Reagents and chemicals

All solutions were prepared with nanopure water (Barnstead) and all chemicals were reagent grade or purer. Preparation of the $\text{Ca}(\text{NO}_3)_2$ stock solution from CaCO_3 , of the NaClO_4 stock solution in water and of the 0.15 M (i.e. 1%) HNO_3 eluent were as previously described [5].

For use in the sorption rate studies of Ca^{2+} on CPG–Oxine and CPG and in the sorption rate study of Na^+ on CPG–Oxine, the single solution contained $2.00 \cdot 10^{-5}$ M Ca^{2+} , 0.0100 M 4-(2-hydroxyethyl)-1-piperazineethanesulphonic acid (HEPES) buffer and 0.0200 M NaClO_4 . It was prepared from stock solutions, adjusting its pH to 7.0₀ with ammonia water. This solution had an ionic strength of 0.0224 M.

For use in the equilibrium Na^+ -sorption study, a series of solutions was prepared which contained $2.00 \cdot 10^{-5}$ M Ca^{2+} with various concentrations of NaClO_4 between 0.00100 and 0.140 M. These solutions contained no HEPES buffer but, rather, were adjusted to pH 7.0₀ using NaOH and HNO_3 . Since no buffer was used, the pH was checked frequently in both the solution in the reservoir bottle and in the effluent from the CPG–Oxine column.

Batch 850605085 of CPG–Oxine and batch 860313081 of underivatized CPG (Pierce Chemical) were used in this work [1,4,5].

2.2. Apparatus

The column equilibration apparatus has been described [5]. The “column” was a small (ca. 4.5 mm × 2.1 mm I.D.) bed of either CPG–Oxine (5.4 mg) or CPG (4.7 mg) that was present in the central hole of the Kel-F slider of a modified injection valve. It was thermostatted at $25 \pm 1^\circ\text{C}$. All other apparatus, such as pH meter, peristaltic pump, Model 4000 spectrometer (Perkin Elmer) for atomic absorption of Ca^{2+} , and Model AA-10 spectrometer (Varian) for flame

atomic emission of Na^+ were as before [5]. The acid eluate from the column was led directly into the flame of the spectrometer via a PTFE capillary tube so that the atomic absorption signal for Ca^{2+} and the atomic emission signal for Na^+ were in the form of a peak, the area of which was measured with a digital integrator.

2.3. Ca^{2+} sorption rate study

The sorption rate of Ca^{2+} was measured on both CPG–Oxine and CPG. Briefly, the solution containing $2.00 \cdot 10^{-5}$ M Ca^{2+} , 0.0100 M NH_4^+ HEPES buffer (pH 7.00) and 0.0200 M NaClO_4 was pumped through the bed of either CPG–Oxine or CPG for various periods of time between about 2 and 250 min (the loading time), after which 0.15 M HNO_3 was used to elute Ca^{2+} from the column into the atomic absorption spectrometer (the elution step). Although all of the Ca^{2+} eluted from the column in less than the 1-min integration time, the elution step was continued for a total of 4 min. After calibrating the spectrometer by injecting various concentrations of Ca^{2+} standard solution, the areas of the eluted Ca^{2+} peaks were used to calculate the amount of Ca^{2+} sorbed by the column during the loading time. In this type of experiment the amount of Ca^{2+} in the column hold-up volume (17 μl) must be subtracted from the amount eluted in order to determine the amount sorbed [11,12]. In the Ca^{2+} sorption rate study on CPG–Oxine the hold-up volume correction was less than 2% of the equilibrium amount of sorbed Ca^{2+} . In the study on CPG the hold-up volume correction varied from a low of 11% at the 2-min point to a high of 20% at the 240-min point.

After the acid elution step the column was washed with water and was then ready for loading of the next sample.

2.4. Na^+ sorption rate study

The procedure for measuring the rate of Na^+ sorption on CPG–Oxine is similar to the Ca^{2+} sorption rate procedure except that a washing

step is interposed between the loading and elution steps. Immediately following the loading step the column was washed for 30 s with sodium-free 0.0200 M NH_4^+ HEPES buffer (pH 7.00) in order to wash out all of the Na^+ -containing interstitial and pore solution. Following the HEPES washing step the column was eluted for 4.00 min with 0.15 M HNO_3 in order to remove all of the strongly sorbed Na^+ and transfer it to the atomic emission spectrometer. Although area integration was performed for the full 4 min, nearly all of the Na^+ eluted within 90 s.

2.5. Na^+ sorption equilibrium study

This new set of experiments was performed on the CPG–Oxine column. A solution containing $2.00 \cdot 10^{-5}$ M of Ca^{2+} and various concentrations of NaClO_4 at pH 7.0₀ was pumped through the column for a sufficiently long time that sorption equilibrium was achieved. Both 2- and 4-h loading times were employed in order to verify that equilibrium was reached. Immediately following this loading step the column was washed with 0.00100 M NH_4^+ HEPES (pH 7.00, Na^+ -free) for 30 s. Then it was eluted for 4.00 min into the atomic emission spectrometer with 0.15 M HNO_3 .

In order to compensate for possible drift in instrument sensitivity and solution composition over the long periods of time involved in the loading studies, Na^+ calibrations were performed both before and after each experimental run. A series of Na^+ standards was injected using valve V2 (Fig. 2 in Ref. [5]), both before and after each experimental point, and averages for the standards were used in the calculations.

3. Results and discussion

Three aspects of the behavior of CPG–Oxine arising from the ionization of silanol groups on the surface and in the hydrated gel layer are quantified. First, the equilibrium sorption of Na^+ by CPG–Oxine is characterized. Second, a quantitative electrical double-layer model is de-

veloped in which the complexation of Ca^{2+} by immobilized oxinate ligand is related to sorption of Na^+ in the hydrated layer via the electrical potential ψ_x . Finally, the desorption rate of Ca^{2+} from CPG–Oxine is quantified as a function of the potential ψ_x in order to validate the model.

3.1. Equilibrium sorption of Na^+

In this study, the CPG–Oxine column was equilibrated with pH = 7.0₀ solutions containing various concentrations of Na^+ , as the ClO_4^- salt, in the range $[\text{Na}^+] = 0.00100$ to 0.140 M. The solutions also contained $2.00 \cdot 10^{-5}$ M of Ca^{2+} , but the small amounts of Ca^{2+} both in solution and sorbed on CPG–Oxine can be ignored in this study of Na^+ sorption. Establishment of equilibrium was verified by finding the same results when the experiments were performed for both a 2- and a 4-h loading time. The concentration of Na^+ sorbed at equilibrium, $\bar{N}_{\text{Na, equil}}$ (mmol/g) is plotted versus $[\text{Na}^+]$ in Fig. 1, where it is seen that the amount of sorbed Na^+ increases toward a limiting value. This plot is a sorption isotherm for Na^+ . The data are presented in Table 1. The sorption isotherm,

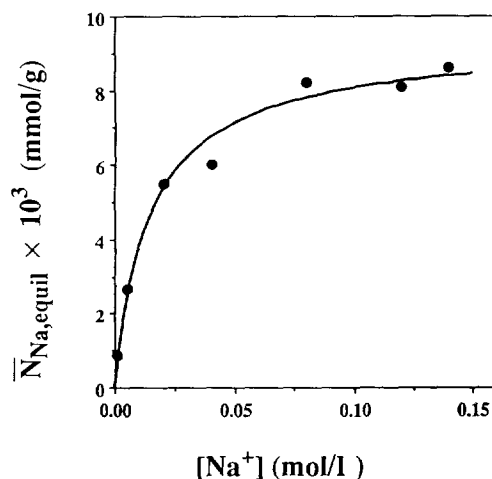


Fig. 1. Sorption isotherm of Na^+ on CPG–Oxine from pH 7.0₀ bulk solution. The points are experimental data. The line is predicted from Eq. 1 using $K = 74$ l/mol, $(\text{SiO}^-)_0 = 9.61 \cdot 10^{-3}$ mmol/g and γ_{Na} from Table 1, as discussed in the text.

butes to $\overline{(\text{SiONa})}$ only when it has passed through the surface and entered into the hydrated layer, in which it “neutralizes” an equivalent number of SiO^- groups. The term “sorption” as used for Na^- here does not imply “site-binding” of Na^+ .

In contrast, SiO^- groups at the surface lie in a plane that is well separated from the plane of closest approach of Na^+ ions in solution in the diffuse part of the electrical double layer. It is in the diffuse layer that is to be found the remainder of the “surface excess” of Na^+ , equal in number to the remaining “unneutralized” SiO^- groups in the hydrated layer and at the surface. Since the diffuse layer is in the pore liquid these Na^+ ions would not be detected in this experiment because the pore liquid is washed out with NH_4^+ solution prior to the acid-elution step. Thus, the results of the previous titration experiments combined with the results of the present Na^+ -sorption experiment show that, at pH 7.0, about one-third (i.e. 0.0096/0.027) of the ionized silanol groups lie within the hydrated layer and about two-thirds are to be found at the glass surface. These SiO^- groups at the glass surface represent about 3% of the number of SiOH groups at the glass surface [14–17]. (Since only a small fraction of the surface silanols have been derivatized with 5-phenylazo-8-hydroxyquinoline groups [1], derivatized silanols have been omitted from the discussion.)

It should be noted that the sorption of Na^- into the hydrated layer arises because H^+ ions have left that region, leaving behind excess negative charge. This phenomenon is therefore an “ion-exchange” process. However, complete 1:1 stoichiometric exchange of Na^- for H^+ in the hydrated layer is not required; and evidently is not achieved at $[\text{Na}^+]$ below 0.15 M Na^+ , as seen in Fig. 1. The reason why stoichiometric ion exchange is not required is because the hydrated layer is so thin (i.e. tens of Å, Ref. [5]) that local electroneutrality may be violated within it. This is simply another way of saying that part of the equilibrium “surface excess” of negative SiO^- groups lies within the hydrated layer, in addition to the part which lies in the surface plane. (Naturally, local electroneutrality is also violated

within the diffuse part of the double layer in the adjacent solution, which contains a “surface excess” of positive charge that is exactly equal to the sum of the excesses of negative charge in both the hydrated layer and the surface plane.)

3.2. Double-layer sorption model for Ca^{2+}

It has been shown that Ca^{2+} is sorbed on CPG–Oxine from a NaClO_4 solution by two different processes [4]. One sorption process is complexation of Ca^{2+} by the immobilized oxinate ligand, the extent of which depends on the electrical potential, as discussed above. This process is specific “site-binding” of Ca^{2+} . The other sorption process probably is related to cation exchange of Ca^{2+} for Na^+ in the diffuse part of the electrical double layer. (There is no evidence to suggest that Ca^{2+} enters the hydrated layer.) The former of these two processes, complexation, is generally much more important than the latter.

The oxinate moiety of the bound 5-phenylazo-8-hydroxyquinoline, which is the anionic bidentate ligand that complexes Ca^{2+} , is located in the solution in the diffuse part of the electrical double layer at a distance of X cm from the glass surface. It is the electrical potential ψ_x (V), at location X which influences the Ca^{2+} complexation by oxinate. The bound oxine thus acts as a probe of the potential at the location X cm from the surface.

According to the “ionizable surface group, site-binding model” [5], the millimoles of Ca^{2+} complexed per gram of CPG–Oxine, \bar{N}_{Ca} , is related to ψ_x by the expression:

$$\bar{N}_{\text{Ca}} = [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}} \cdot \bar{\alpha}_{\text{ox}} \cdot \bar{\nu}_{\text{oxine}} \cdot \bar{\beta}_1 \cdot \exp\left(-\frac{2F\psi_x}{RT}\right) \quad (2)$$

in which R is the ideal gas constant [8.314 J/(molK)]; F is the Faraday constant (96 487 C/equiv); T is absolute temperature; $[\text{Ca}^{2+}]$ is the bulk solution concentration (M); γ_{Ca} is the bulk solution ionic activity coefficient of Ca^{2+} ; $\bar{\alpha}_{\text{ox}}$ is the fractional ionization of immobilized oxine as oxinate; $\bar{\nu}_{\text{oxine}}$ is the complexation capacity of

CPG–Oxine which is $(3.6 \pm 0.5) \cdot 10^{-6}$ mmol/g [1]; and $\bar{\beta}_1$ is the formation constant of the 1:1 complex between Ca^{2+} and immobilized oxinate (i.e. $5 \cdot 10^3$ l/mol, Ref. [4]), with all concentrations taken at location X in the diffuse layer. The values of $\bar{\nu}_{\text{oxine}}$ and $\bar{\beta}_1$ are constants.

The value of $\bar{\alpha}_{\text{ox}}$ depends on the value of ψ_x . When ψ_x becomes less negative it causes the local pH at position X to increase which causes $\bar{\alpha}_{\text{ox}}$ to increase. The relationship is derived as follows: $\bar{\alpha}_{\text{ox}}$ is defined in terms of both the activity of H^+ in the bulk solution, $a_{\text{H}} = 1.0 \cdot 10^{-7} M$, and the acid dissociation quotient for the phenolic hydroxyl group on the immobilized oxine, \bar{K}'_{a2} [1,4]:

$$\bar{\alpha}_{\text{ox}} = \frac{\bar{K}'_{\text{a2}}}{a_{\text{H}} + \bar{K}'_{\text{a2}}} \quad (3)$$

The acidity quotient \bar{K}'_{a2} is related to the acidity constant (\bar{K}_{a2}), given in terms of the activity of H^+ , by the following expression [1]:

$$\bar{K}'_{\text{a2}} = \bar{K}_{\text{a2}} \cdot \exp\left(+\frac{F\psi_x}{RT}\right) \quad (4)$$

Combining Eqs. 3 and 4 and taking into account the fact that at pH = 7, $a_{\text{H}} \ll \bar{K}'_{\text{a2}}$ gives the following expression:

$$\bar{\alpha}_{\text{ox}} \approx \bar{K}_{\text{a2}} \cdot a_{\text{H}}^{-1} \cdot \exp\left(+\frac{F\psi_x}{RT}\right) \quad (5)$$

Substituting for $\bar{\alpha}_{\text{ox}}$ from Eq. 5 into Eq. 2, rearranging and taking the natural logarithm of both sides yields the expression:

$$\ln\left(\frac{\bar{N}_{\text{Ca}}}{\gamma_{\text{Ca}}}\right) = \ln\left([\text{Ca}^{2+}] \cdot \bar{\nu}_{\text{oxine}} \cdot \bar{\beta}_1 \cdot \bar{K}_{\text{a2}} \cdot a_{\text{H}}^{-1}\right) - \frac{F \cdot \psi_x}{RT} \quad (6)$$

From Eq. 6 it is predicted that a plot of $\ln(\bar{N}_{\text{Ca}}/\gamma_{\text{Ca}})$ versus ψ_x should be linear with slope of $-F/RT$ (i.e. -38.9).

The potential at distance x , ψ_x , can be calculated from the potential at the surface, ψ_0 , using the following series of expressions [18,19]:

$$\psi_x = \frac{2RT}{ZF} \cdot \ln \frac{1 + \gamma_{\text{GC}} \cdot \exp(-\kappa X)}{1 - \gamma_{\text{GC}} \cdot \exp(-\kappa X)} \quad (7)$$

where

$$\gamma_{\text{GC}} = \frac{\exp\left(\frac{ZF\psi_0}{2RT}\right) - 1}{\exp\left(\frac{ZF\psi_0}{2RT}\right) + 1} \quad (8)$$

and

$$\kappa = \left(\frac{2000Z^2F^2}{\epsilon_0 DRT}\right)^{1/2} \cdot c^{1/2} \quad (9)$$

In these expressions Z has the value one (with no sign), ϵ_0 is the permittivity of a vacuum ($1.12 \cdot 10^{-12}$ C/V·cm), D is the dimensionless dielectric constant of water divided by 4π (i.e. $78.3/4\pi$), and c is the ionic strength of the bulk solution (M). Since Ca^{2+} is present at trace-level concentrations, its contribution, both in the complexed state and as an electrolyte component in solution, can be neglected. For this reason, the Gouy–Chapman treatment for uni-univalent electrolytes, with $Z = 1$, is appropriate.

The question then becomes how to calculate the surface potential, ψ_0 . Previously, the relatively simple “surface ionization model” was used [1,4,5], in which it was assumed that the ionized silanolate groups are present only at the two-dimensional glass surface located at the interface between the hydrated layer and the solution [1,2,4–6,9]. This simple model is inconsistent with the “porous gel” assumption which has been invoked to explain the excessively slow sorption of Na^+ by CPG [5] and which has been described above. In a porous gel [6,20,21], ionization of silanol groups occurs throughout the hydrated layer which has a thickness in the range of tens of Å units [22]. The simple “surface ionization” model, which was previously used, can be treated mathematically by the relatively simple Gouy–Chapman theory of the electrical double layer in order to obtain ψ_0 , while in contrast, the porous gel model involves a double-diffuse double layer, for which the theoretical calculation of ψ_0 is more complex [6,20,21]. Although the evidence favors the view that a porous gel model should be used to calculate ψ_0 , it is not possible to do so with the information that is available on the properties of CPG–Oxine. Therefore, as an approximation,

the system will be treated using the simpler “surface ionization model”. That is, although some of the anionic silanolate groups are distributed throughout the hydrated porous gel layer, across a distance in the range of tens of Angstroms, for purposes of calculating their contribution to ψ_o all of the silanolate groups will be treated as though they reside at the surface of the hydrated layer. The Gouy–Chapman theory will be employed. A result of this approximation is that the calculated values of the surface potential, ψ_o , and of the potential at the location of oxine, ψ_x , will be somewhat higher than their true values.

According to the Gouy–Chapman theory, the potential at the surface is given by the expression:

$$\sinh\left(\frac{ZF\psi_o}{2RT}\right) = (8.53 \cdot 10^4) c^{-1/2} \sigma_o \quad (10)$$

where σ_o is the charge density (C/cm^2) due to silanolate groups [19,23,24]. The charge density is related to the excess concentration of negatively charged groups on the glass, Q_t (mmol/g), as follows:

$$\sigma_o = \frac{Z_- F Q_t}{1000 A_{sp}} \quad (11)$$

Here Z_- has the value -1 . The quantity Q_t is equal to the concentration of ionic silanolate groups (i.e. concentration of protons that have left both from within and from the surface of the hydrated layer) *minus* the concentration of Na^+ ions that have entered into the hydrated layer.

3.3. Sorption/desorption rate of Ca^{2+}

Shown in Fig. 2 is a diagrammatic representation of the interfacial region during the time that the slow sorption of Na^+ is taking place. Initially, the CPG–Oxine was washed with dilute acid followed by water. Then the pH and the ionic strength were raised by contacting it with a sample solution containing fixed concentrations of buffer, $NaClO_4$ and Ca^{2+} . As discussed above, some fractions of the silanol groups in the porous gel layer and at the surface ionize to form silanolate and hydrogen ions. The dissociated

hydrogen ions diffuse out of the gel layer at a relatively rapid rate. The “surface excess” of negative SiO^- is the sum of SiO^- at the surface and within the hydrated layer. Gradients of negative electrical potential become established both in the porous gel layer and in the diffuse layer in the adjacent pore liquid.

During this short period of time when dissociated H^+ is rapidly diffusing out of the gel layer and out of the pore liquid into the solution surrounding the CPG–Oxine particle, Ca^{2+} is diffusing to the location X and complexing with the oxinate ligand in order to satisfy the increasingly negative value of ψ_x in Eq. 2. This series of processes leading to the sorption of increasing amounts of Ca^{2+} is completed in about 1 to 2 min, as seen from the rising part of the curve in Fig. 3A in Ref. [5]. Because the diffusion time of H^+ in the gel layer and of both H^+ and Ca^{2+} in the pore solution are all comparable to one another, data obtained at $t \leq 1$ to 2 min do not reveal their rates of diffusion, other than to show that they are all relatively fast.

Now, at a rate much slower than that at which H^+ ions diffused out, Na^+ ions diffuse into the gel layer until equilibrium is established. This is seen in Fig. 6B of Ref. [5]. That is, the establishment of Na^+ sorption equilibrium within the hydrated layer is a slow process. If $\bar{N}_{Na,t}$ (mmol/g) is the concentration of Na^+ sorbed at time t , then the concentration of ionic silanolate groups, Q_t , at time t is:

$$Q_t = Q_{max} - \bar{N}_{Na,t} \quad (12)$$

where Q_{max} has the value of 0.0270 mmol/g. After only 2 min of loading, the H^+ produced by the ionization of $SiOH$ groups has diffused out of the hydrated layer, but very little Na^+ has diffused in. That is, for $t = 2$ min, $\bar{N}_{Na,t} \approx 0$ and $Q_t \approx Q_{max}$. With time, Q_t continues to decrease as more Na^+ diffuses in, and this decrease in Q_t decreases σ_o which, in turn, makes ψ_o and ψ_x less negative and consequently decreases \bar{N}_{Ca} . This is seen from the Ca^{2+} rate curves in Fig. 3B and in Fig. 6A, both in Ref. [5]. After a sufficiently long time $\bar{N}_{Na,t}$ has increased to its constant equilibrium value $\bar{N}_{Na,eq}$ and as a consequence

\bar{N}_{Ca} has decreased (i.e. desorbed) to its equilibrium value. Kinetically, it is assumed that the rates of formation and dissociation of the 1:1 Ca^{2+} -oxinate complex are much faster than the rate of Na^+ sorption into the hydrated layer.

Data for the rates of Na^+ sorption and Ca^{2+} sorption/desorption are taken from Ref. [5]. Based on the above discussion, the time 2.0 min from the start of the experiment is taken to be $t=0$ min in both the Na^+ - and Ca^{2+} - rate experiments. The first column in Table 2 presents the times at which Na^+ sorption was measured experimentally on CPG-Oxine and the second column presents the experimentally measured amounts of Na^+ sorbed at those times.

In the third column are shown the amounts of Ca^{2+} sorbed on CPG-Oxine at the same times. Since Ca^{2+} sorption was measured experimentally at times not identical to those in the first column of Table 2, the amounts of Ca^{2+} sorbed that are shown in the third column were calculated from the least-squares curve fit to the data in Ref. [5]. The first order equation (starting $t=0$ at 2 min) which describes the Ca^{2+} desorption rate on CPG-Oxine is:

$$\bar{N}_{Ca}(\text{CPG-Oxine}) = (5.94 \pm 0.07) \cdot 10^{-4} - 2.275 \cdot 10^{-4} \{1 - \exp[(-0.0273 \pm 0.0011) \cdot t]\} \quad (13)$$

The correlation coefficient is $r=0.994$. Uncertainties are standard deviations.

In order to identify the amount of Ca^{2+} that is sorbed onto CPG-Oxine by processes other than complexation with immobilized oxinate, Ca^{2+} sorption by CPG (with no oxine) was also measured (Fig. 3C in Ref. [5]). The amount of Ca^{2+} sorbed on CPG is about 10% of the amount sorbed on CPG-Oxine and, taking 2 min to be zero time, its amount, $\bar{N}_{Ca}(\text{CPG})$, is given as a function of time by the equation:

$$\bar{N}_{Ca}(\text{CPG}) = (5.71 \pm 0.05) \cdot 10^{-5} - (1.15 \pm 0.04) \cdot 10^{-7} \cdot t \quad (14)$$

which has a correlation coefficient of $r=0.997$. Values of $\bar{N}_{Ca}(\text{CPG})$ are presented in the fourth column of Table 2. Because such a small fraction of the silanol groups on the surface of CPG-Oxine is derivatized with oxine, it can be assumed that at any time t the amount of Ca^{2+} sorbed on CPG-Oxine by processes other than complexation with oxinate is equal to $\bar{N}_{Ca}(\text{CPG})$. Thus, the value of \bar{N}_{Ca} , corresponding to Ca^{2+} sorbed on CPG-Oxine only by complexation with oxinate, is given by the expression:

$$\bar{N}_{Ca} = \bar{N}_{Ca}(\text{CPG-Oxine}) - \bar{N}_{Ca}(\text{CPG}) \quad (15)$$

Table 2

Parameters relating to the sorption of Ca^{2+} and Na^+ from a solution containing $2.00 \cdot 10^{-5}$ mol/l Ca^{2+} and 0.0200 mol/l Na^+ at pH 7.00 and ionic strength 0.0224 M employing $X=5.7 \cdot 10^{-8}$ cm and $\gamma_{Ca}=0.549$

t^a (min)	$\bar{N}_{Na,t}^b$ (mmol/g)	$\bar{N}_{Ca}(\text{CPG-Oxine})^c$ (mmol/g)	$\bar{N}_{Ca}(\text{CPG})^d$ (mmol/g)	\bar{N}_{Ca} (mmol/g)	Q_1 (mmol/g)	σ_o (C/cm ²)	ψ_o (V)	ψ_x (V)	$\ln(\bar{N}_{Ca}/\gamma_{Ca})$
0	0	$5.94 \cdot 10^{-4}$	$5.71 \cdot 10^{-5}$	$5.37 \cdot 10^{-4}$	0.0270	$-3.72 \cdot 10^{-6}$	-0.0768	-0.0536	-6.93
3	$0.926 \cdot 10^{-3}$	$5.77 \cdot 10^{-4}$	$5.68 \cdot 10^{-5}$	$5.19 \cdot 10^{-4}$	0.0261	$-3.59 \cdot 10^{-6}$	-0.0752	-0.0526	-6.96
14	$1.67 \cdot 10^{-3}$	$5.22 \cdot 10^{-4}$	$5.55 \cdot 10^{-5}$	$4.66 \cdot 10^{-4}$	0.0253	$-3.49 \cdot 10^{-6}$	-0.0739	-0.0518	-7.07
28	$3.74 \cdot 10^{-3}$	$4.72 \cdot 10^{-4}$	$5.39 \cdot 10^{-5}$	$4.19 \cdot 10^{-4}$	0.0233	$-3.20 \cdot 10^{-6}$	-0.0700	-0.0495	-7.18
62	$7.89 \cdot 10^{-3}$	$4.08 \cdot 10^{-4}$	$5.00 \cdot 10^{-5}$	$3.58 \cdot 10^{-4}$	0.0191	$-2.63 \cdot 10^{-6}$	-0.0614	-0.0441	-7.33
116	$8.81 \cdot 10^{-3}$	$3.76 \cdot 10^{-4}$	$4.38 \cdot 10^{-5}$	$3.32 \cdot 10^{-4}$	0.0182	$-2.51 \cdot 10^{-6}$	-0.0593	-0.0427	-7.41
179	$9.30 \cdot 10^{-3}$	$3.68 \cdot 10^{-4}$	$3.65 \cdot 10^{-5}$	$3.32 \cdot 10^{-4}$	0.0177	$-2.44 \cdot 10^{-6}$	-0.0582	-0.0420	-7.41
244	$9.44 \cdot 10^{-3}$	$3.67 \cdot 10^{-4}$	$2.90 \cdot 10^{-5}$	$3.38 \cdot 10^{-4}$	0.0176	$-2.42 \cdot 10^{-6}$	-0.0578	-0.0417	-7.39

^a Real time for Na^+ sorption minus 2 min.

^b Experimental data points for Na^+ sorption on CPG-Oxine at times t .

^c From Eq. 13, describing experimental Ca^{2+} sorption rate on CPG-Oxine.

^d From Eq. 14, describing experimental Ca^{2+} sorption rate on CPG.

Values of \bar{N}_{Ca} are presented in the fifth column.

In the sixth, seventh and eighth columns of Table 2 are presented the values of Q_t , σ_o and the surface potential ψ_o which were calculated from Eqs. 12, 11 and 10, respectively. In the last column are shown values of the function $\ln(\bar{N}_{Ca}/\gamma_{Ca})$. The activity coefficient γ_{Ca} is 0.549 [4], which is constant because the ionic strength of the bulk solution is constant.

Eq. 6 describes the relationship between the amount of Ca^{2+} sorbed via complexation by oxinate on CPG–Oxine and the potential ψ_x . The other parameters in Eq. 6, $[Ca^{2+}]$, γ_{Ca} , \bar{v}_{oxine} , $\bar{\beta}_1$ and \bar{K}_{a2} , are constants which would appear in the intercept of the plot of $\ln(\bar{N}_{Ca}/\gamma_{Ca})$ versus ψ_x . The difficulty in making such a plot is the fact that the value of X , which is required in Eq. 7 to calculate ψ_x , is not known. However, it can be obtained by trial and error. A value is assumed for X and is used in Eq. 7 to calculate ψ_x as a function of time. A plot is made of $\ln(\bar{N}_{Ca}/\gamma_{Ca})$ vs. ψ_x . The procedure is repeated for various assumed values of X . The correct value of X is the one which leads to a straight line plot with a slope of -38.9 (i.e. $-F/RT$). For the present system, X is found to be $(5.7 \pm 1.1) \cdot 10^{-8}$ cm (i.e. 5.7 \AA). The corresponding values of ψ_x from Eq. 7 are presented in column 9 of

Table 2 and the plot of $\ln(\bar{N}_{Ca}/\gamma_{Ca})$ vs. ψ_x is shown in Fig. 3. It is linear with a correlation coefficient $r = 0.98$, a slope of -38.9 ± 2.9 and an intercept of -9.06 ± 0.14 . The uncertainty in X is estimated from the uncertainty in the slope.

An experimental value of about 6 \AA for X is quite reasonable since the spacer-arm which attaches the oxinate ligand to the glass surface, when fully extended, would place the oxinate about 18 \AA away from the surface [1,25]. Thus, an observed value of $X \approx 6 \text{ \AA}$ suggests that at pH 7 and $c \approx 0.02$ the spacer-arm is folded back on itself, as has previously been suggested [1].

4. Conclusions

Using the immobilized ligand oxine it has been demonstrated that, above the pH of zero charge of the CPG, the surface potential ψ_o and the potential at any location X in the diffuse layer undergo a slow decrease in magnitude of their negative value with time and eventually reach equilibrium values. This slow drift in ψ_o and ψ_x results from the slow sorption of Na^+ , presumably as a result of diffusion of Na^+ into the hydrated gel layer.

The potentials ψ_o and ψ_x both correlate strongly with the electrokinetic ζ -potential at the plane of shear. There is considerable interest in the ζ -potential at the surface of fused silica as it relates to electroosmotic flow in the capillaries that are used for capillary electrophoresis. For example, in a recent study of electroosmosis, the results were interpreted in terms of the formation of a complex between alkali metal ions (e.g. Li^+ and Na^+) and SiO^- groups at the surface of the fused silica [26]. The bound alkali metal was assumed to occupy the Inner Helmholtz Plane rather than to enter a hydrated layer. However, it was mentioned that "to ensure equilibrium was reached between the silica and solution phases, the phosphate buffer... was loaded into the capillary at least 6 h before the measurements were carried out." [26]. In addition, it is often observed that long periods of "conditioning" are required for electroosmotic behavior to stabilize

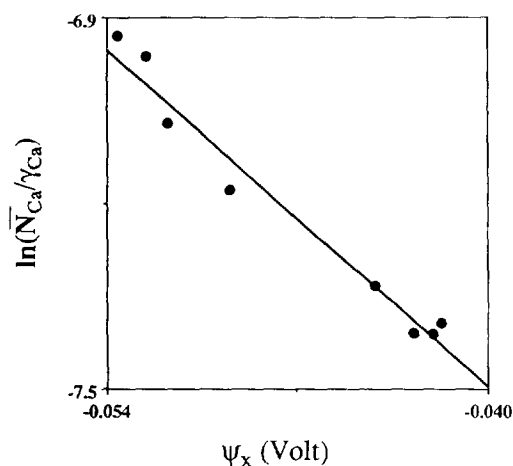


Fig. 3. Plot of $\ln(\bar{N}_{Ca}/\gamma_{Ca})$ vs. ψ_x to test the linear dependence predicted by Eq. 6. Points are data from columns 9 and 10 in Table 2. Oxinate is located at $X = 5.7 \cdot 10^{-8}$ cm. The line is a linear least-squares fit having a slope of -38.9 .

when electrolytes are first put into fused-silica capillaries. Since CPG is a Vycor-type glass that is composed of $\geq 95\%$ SiO_2 , it might be expected that there would be some strong similarities between CPG and fused silica. In fact, a hydrated gel layer is known to form on fused silica [6,22]. Thus, it is likely that slow diffusion of ions such as Na^+ would occur into the hydrated layer on fused silica to produce a slow drift of ζ toward an equilibrium value after, for instance, an electrolyte of higher pH has been introduced into the capillary. This interpretation of the slow "conditioning" of fused silica seems more likely than adsorption of such ions into an Inner Helmholtz Plane, located at the boundary between the silica capillary-surface and the solution, because the latter should not be a particularly slow process.

Finally, it may be noted that when the surface potential, ψ_0 is ≤ 0.025 V the so-called Debye-Hückel (D-H) approximation can be made. With this approximation the hyperbolic sine-term on the left-hand side of Eq. 10 simplifies to $(ZF\psi_0/2RT)$, so that Eq. 10 becomes [18]:

$$\psi_0 \approx \frac{(8.53 \cdot 10^4)2RT}{ZF} \cdot \sigma_0 \cdot c^{-1/2} \quad (16)$$

Also as a result of the D-H approximation, Eq. 7 simplifies to the form [1,4,18]:

$$\psi_x \approx \psi_0 \cdot \exp(-3.29 \cdot 10^7 c^{1/2} X) \quad (17)$$

Combining Eqs. 11, 16 and 17 shows that when $\psi_0 \leq 0.025$ V, at 25°C, ψ_x can be expressed as:

$$\psi_x \approx -\frac{4.38 \cdot 10^3 F c^{-1/2}}{1000 A_{sp}} Q_t \cdot \exp(-3.29 \cdot 10^7 c^{1/2} X) \quad (18)$$

That is, ψ_x becomes directly proportional to Q_t , the sum of charge on the surface plus hydrated gel layer. Then Eq. 6 can be replaced by an expression of the form:

$$\ln \frac{\bar{N}_{Ca}}{\gamma_{Ca}} = A + B \cdot Q_t \quad (19)$$

where A and B are constants.

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6. References

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