Surface Chemical Aspects of Coagulation, Deposition, and Filtration Processes :
Variation of Electrokinetic Potential at Metal Oxide-Water and Organic-Water Interfaces in the Na$^+$ and Ca^{2+} Ion Solutions

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This study measured the zeta potential of both latex colloidal particles with carboxylate surface groups and glass beads (collectors) with silanol surface group employing various solution with different chemical characteristics. The results have been compared with the surface chemistry theory.

The zeta potential of the particle and collector increased with increasing pH up to 5.0 regardless of the solution chemistry. For a monovalent electrolyte solution(sodium chloride solution) the zeta potential steadily increased until the pH reached 9.5. In contrast, little change in zeta potential was made between 5.0 and 9.5 for a divalent electrolyte solution (calcium chloride solution). In other words, the more the pH decreases, the larger the effect of neutral salts, such as NaCl and CaCl$_2$, have on the ζ-potential values. In this study, the PZPC(point of zero proton condition) of the particle and collector occurred below a pH of 3.0, H$^+$ and OH$^-$ acted as a PDI (potential determining ion), and Na$^+$ acted as an IDI(indifferent ion).

The magnitude of the negative ζ-potential values of the particle and collector monotonically increased as the concentrations of Na$^-$ or Ca^{2-}([Na$^-$] or [Ca^{2-}]) decreased (the values of pNa or pCa increased). In the case of latex particles, the ζ-potential should approach zero (isoelectric point; IEP) asymptotically as the pNa approaches zero, while in the case of calcium chloride electrolyte, ζ-potential reversal may be expected to occur around 3.16×10^{-2} M CaCl$_2$ (pCa=1.5).

pH, valance and ionic strength can be used in various ways to improve the water treatment efficiency by modifying the charge characteristics of the particle and collector. Predictive capability is far less certain when EDL(electrical double layer) repulsive forces exist between the particle and collector.

Key words : ζ-potential, surface chemistry, specific adsorption, EDL, IDI, IEP, PDI, PZPC

1. Introduction

1.1. Problem Statement and Significance

In most water treatment processes, the rate-controlling step can be either a chemical step such as surface properties of the solid particles and a complexation at the solid-water interface, i.e., attachment of a specific chemical species onto a surface of defined composition or a physical (transport) step such as hydrodynamics and external forces. A chemical step is apparently limiting in almost all drinking water treatment processes, including precipitation, coagulation, water filtration, adsorption, ion exchange, and chemical oxidation-reduction reactions with the exception of adsorption onto activated carbon and certain ion exchange reactions(Bales, 1986).

When two solid particles come close together,

their EDLs(electrical double layers) begin to interact. When both EDLs have charges of similar sign, a repulsive force is generated that increases as the separating distance decreases. Attachment is possible due to the LVDW(London-van der Waals) attractive forces. When they have charges of opposite sign, particle-collector and particle-particle associations are favorable. In the attachment step, the dominant force is the EDL interaction force(McDowell-Boyer et al., 1986). In such situations the influence of solution chemistry on solid surface properties is treated experimentally by incorporating measurements of zeta potential (ζ-potential) into theoretical models for the calculation of the EDL interaction force. The zeta potential is characterized by the nature of the interfacial region between a solid and the bulk solution(Hohl et al., 1980).

Changes in solution chemistry may destabilize solid particles so that they flocculate and attach to a collector as aggregates via LVDW attractive forces. Destabilization may be accomplished by compression of the diffuse layer of charge surrounding the solid particles by a high concentration of inert electrolyte, by pH adjustment to the point of zero particle surface charge, or by the presence of counterions that preferentially adsorb onto particles and decrease the net surface charge so that attractive forces dominate(McDowell-Boyer et al., 1986).

Solid surfaces of primary interest are those on suspended particles—metal oxides, silicates, carbonates, organics, or some combination of these—sand filter grains, or particles formed from addition of chemicals. Very little is known about the mineral identity of particles in water or about the chemical behavior of their surfaces(Bales, 1986).

Oxides, especially those of Si, Al and Fe, are abundant components of the earth's crust. Hence such oxides, or hydroxides, are common constituents of most colloidal particles in natural waters. The dominant role of dissolved NOM (natural organic matter) in determining particle surface properties has been shown for suspended and colloidal material in seawater(Hunter and Liss, 1979) and for selected particles in fresh waters having a NOM concentration above a few milligrams per liter(Davis, 1982 ; Bales, 1984). It is thus plausible that chemical properties of many particles in raw water are determined less by the underlying nature of the mineral than by their organic coating. One exception is silica, which adsorbs smaller amounts of NOM. Because of the influence of organic anions, and because silica surfaces carry a negative charge, positively-charged particles are generally not found in natural waters. Particles formed in water treatment, however, may have an inorganic surface or a mixed organic-inorganic surface(Bales, 1986).

Specific adsorption of cations and anions on hydrous oxide surfaces may be interpreted as surface coordination reactions and is of importance in natural water systems, in geochemical processes, in colloid chemistry, and in water and wastewater treatment systems. The net surface charge of an oxide is sensitive to the composition of the aqueous phase(solution chemistry), because adsorption(i.e., binding) of solutes to the surface of the colloids may increase, decrease, or reverse the effective charge on the solid(Hohl et al., 1980). The net resultant surface charge of an oxide is experimentally accessible from the proton balance at the solid-water interface and from a measurement of the bound unhydrolyzed cation and deprotonated anion. Specifically adsorbed cations will shift the proton condition in such a way as to lower the pH of the PZPC(point of zero proton condition) and shift the IEP(isoelectric point) to higher pH values. Correspondingly, adsorbing anions increase the pH of the PZPC but lower the pH of the IEP (Stumm, 1977).

pH, valance and ionic strength can be used in various ways to improve the water treatment efficiency by modifying the charge characteristics of the particle and collector. Chemical effects on filtration, deposition and coagulation are the result of changes in surface interaction forces due to the specific interaction of ions and molecules with particle and collector surfaces and to changes in ionic strength, that is, chemical effects on them are caused by the combined effects of particle surface chemistry, collector surface chemistry and solution chemistry. Predictive capability is far less certain when EDL repulsive forces exist between particle and collector.

The fact that changes in aqueous chemistry may alter the mobility of particulate matter already residing in an aquifer is an important factor con-

sidered in recharge operations and in the petroleum extraction industry. Permeability reduction in soil systems and porous formations can be caused by ionic strength alterations.

Therefore, to know how much and in what way the solution chemistry affects the surface charge development, some knowledge of the electrical properties of the oxide/water and organic/water interfaces is required.

1.2. Objectives and Scope of Study

The primary purpose of this study was to extend our understanding of the electrokinetic phenomena and chemical effects that influence the coagulation, deposition, and filtration processes. The experimental work reported in this paper is restricted to measuring the zeta potential of the glass beads collectors and the latex particles with carboxyl acid surface groups in solutions of varying chemical chacteristics(pH, [Na^-], and [Ca^{2-}]).

2. MATERIALS AND METHODS

The experimental materials and methods that were employed to measure the zeta potential and streaming potential for the particle and collector, respectively are described below.

2.1. Suspended Particles

Three different sizes of latex particles were utilized in the present study. Latex particles were manufactured by the controlled polymerization of an emulsion or suspension of a suitable organic monomer such as styrene. All of the particles were monodispersed microspheres coated with yellow-green fluorescent dyes. These fluorescent mono-dispersed microspheres contain carboxylate surface functional groups. All the particles were shipped in deionized water, stored at 4℃, and protected from light or freezing. A summary of their properties as provided by the supplier and/or manufacturer is presented in Table 1. The colloidal particle samples for ζ-potential measurements were prepared by diluting the stock colloid solution with various simple electrolyte solutions. In this study latex particles of 0.093μm(std. dev. 0.001μm), 1.16μm(std. dev. 0.012μm) and 9.33μm(std. dev. 0.64 μm) are referred to as the nominal 0.1μm, 1.0μm

Table 1. Properties of latex particles[†] used in this study

PROPERTY	VALUE
Monomers	Styrene
Weight of Polymer(g/cm³ in latex)	0.025
Density of Polymer(g/cm³)	1.05
Refractive Index(@540 nm)	1.59
Fluorescent Dye	Yellow-Green
Excitation(nm)	458
Emission(nm)	540
Surface Group	Carboxylate
Surface Charge	Negative
pH_{PZPC}	2.5~3.0
Potential-Determining Ion	H^+, OH^-

[†] Supplied and manufactured by Polysciences, Inc., Warrington, Pennsylvania

and 10.0μm particles, respectively.

Deionized and glass distilled water(DI water), produced by using a Corning Megapure distillation system, was employed for all experimental works. Concentrated colloid solutions(Original) were diluted to the stock solutions using unaltered DI water. The stock colloid solutions were stored at 4℃ and diluted to the working solutions as needed, using DI water. The pH of DI water was typically near 5.6 indicating equilibrium with atmospheric carbon dioxide.

2.2. Porous Media

The porous media utilized for the streaming potential measurement were comprised of a plug of glass beads. Various properties of the beads as provided by the supplier and manufacturer (Polysciences, Inc., Warrington, Pennsylvania) are presented in Table 2. The beads are manufactured by heating to melting and then annealing various sized fractions of crushed fragments of soda-lime glass (sodium-calcium-magnesium silicate). The beads are specified as being 90% true spheres with less than 5% irregular shaped particles. Three sized glass beads were employed for this study, whose average diameters were approximately 0.13(0.10~

0.15) mm, 0.28(0.25～0.30) mm and 0.63(0.50～

Table 2. Properties of glass beads† for packed column

PROPERTY	VALUE	
Size Utilized(mm)	0.105～0.150(0.130) 0.250～0.300(0.280) 0.500～0.750(0.630)	
Glass Density(g/cm³)	2.48	
Surface Functional Group in Water	>SiOH(Amphoteric Hydroxyl Group)	
Surface Charge	Negative	
pH$_{PZPC}$	2.5～3.0	
Potential-Determining Ion	H⁺, OH⁻	
Kind of Glass	Soda Lime Glass	
Bulk Glass Composition	Component	% by Weight
	SiO_2	72.0
	Na_2O	15.0
	CaO	7.9
	MgO	4.2
	K_2O	0.2
	Al_2O_3	0.3
	Fe_2O_3	0.37
	PbO	0.2

† Supplied and manufactured by Polysciences, Inc., Warrington, Pennsylvania

0.75) mm.

The orginal glass beads were cleaned by soaking in an ultrasonic bath with DI water, 0.02 M NaOH, DI water, 1.0 M H_2SO_4, and DI water successively prior to packing in the porous plug for the streaming potential experiment. After the final rinse, the beads were dried overnight in an oven at 70℃ to 80℃. The glass beads and plug were cleaned and repacked periodically.

2.3. Zeta Potential Measurement

The technique of particle electrophoresis was employed in this study to measure the ζ-potential of the 0.1μm, 1.0μm and 10.0μm latex particles as a function of solution chemistry. The MODEL 501 LASER ZEE METER™ manufactured by Pen Ken, Inc. was used to measure the ζ-potential of the

latex particles by determining the rate at which the particles move in a known electric field. Since a microscope is utilized to observe the particles, it is common to refer to this method as micro-electrophoresis.

2.4. Streaming Potential Measurement

The apparatus utilized to measure the streaming potential consisted of a solution reservoir, constant head tank, porous plug with Ag-AgCl electrodes, and ion-meter(Model 701A digital Ionalyzer® manufactured by Orion Research Inc.). A schematic diagram of the apparatus for the streaming potential measurement is presented in Fig. 1.
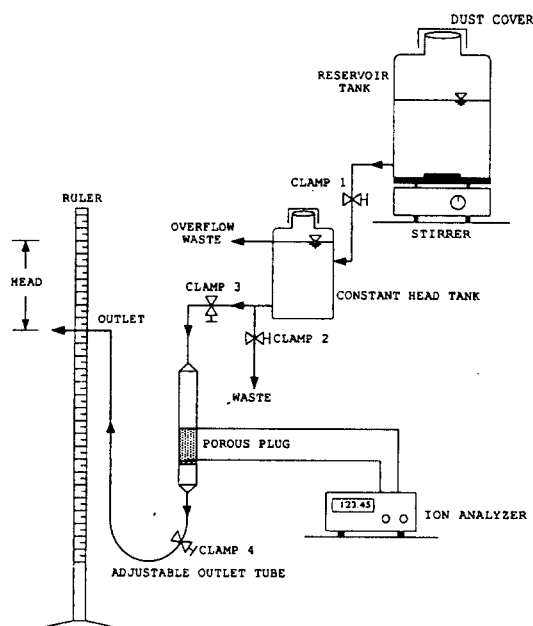

Fig. 1. Schematic diagram of the streaming potential apparatus.

When fluid is forced through a porous plug by external pressure, the charges in the mobile part of the double layer near the solid surface are carried towards one end. As a result, a streaming current develops in the direction of the fluid flow and the potential difference induces a conduction current directed opposite to the fluid flow. Both currents are soon balanced. A streaming potential is equal to a streaming current plus a conduction current.

Typically, a plot of streaming potential versus pressure difference is linear and originates from the origin of the coordinate system. However, the plot does not always intersect the origin due to a difference in the polarization between the two electrodes(background potential). To cancel this polarization in this study, the pressure was instantaneously applied to force the fluid to stream through the porous plug. The simultaneous response, which is ascribed to the streaming potential, was recorded. Streaming potential must be measured under laminar flow conditions or nonlinearlity will be produced. So, four head differences(between the water level of the constant head tank and the outlet tip) such as 2.81, 4.68, 6.55 and 8.42 cmHg were utilized. The streaming potential was measured for only the 0.28 mm sized glass beads because all three sized glass beads had the same properties of soda-lime glass. The values of the ζ-potential of the glass beads were calculated from the streaming potential data using Eq. (1).

$$\zeta = \frac{4\pi\mu K_0 \Delta E_s}{\varepsilon \Delta P} \tag{1}$$

where μ is the absolute viscosity of the medium, ε the electric permittivity of the medium, K_0 the specific conductivity of the liquid, ΔP the pressure difference, and ΔE_s the streaming potential difference.

3. RESULTS AND DISCUSSION

The results of electrokinetic measurements are presented and discussed in this chapter. Values for the ζ-potentials of the glass beads collector were computed from the results of streaming potential measurements. Solution chemistry affects particle and collector ζ-potentials that are used for the calculation of EDL interaction potential. To know how much and in what way the solution chemistry affects ζ-potential, the particle and collector ζ-potentials were both measured in this study.

3.1. Particle Zeta Potential

The ζ-potentials of the three sizes of latex particles(0.1 μm, 1.0 μm and 10.0 μm) were measured for a variety of solution conditions. The results

are illustrated in Figs. 2 and 3. The unit for the ζ-potential values is mV unless otherwise noted.

The ζ-potentials of each size particle, measured as a function of pH from 2.5 to 10.5 in 10^{-3} M (10^{-3} N) NaCl(1:1 electrolyte) and 5×10^{-4} M (10^{-3} N) CaCl$_2$(2:1 electrolyte) are shown in Fig. 2. The results indicate that the particles, except for the 10 μm particles, have a relatively large negative ζ-potential of -60 mV to -80 mV for the solution of NaCl with pH values from 5.0 to 10.5, whereas the particles have almost constant ζ-potential of -30 mV to -40 mV for the solution of CaCl$_2$ with the same pH range. The negative ζ-potential decreases monotonically and significantly as the pH is decreased below a pH of 5.0, reaching values between -15.7 mV and 4.5 mV at a pH of 2.6. These values are for measurements made a few minutes after adding acid and/or base for pH adjustment to the samples being analyzed. The values of ζ-potential of the 0.1μm and 1.0μm particles are approximately same under the same solution chemistry. However, ζ-potential values for the 10.0μm particle in the solution of NaCl differ significantly from those observed for the 0.1μm and 1.0μm particles.

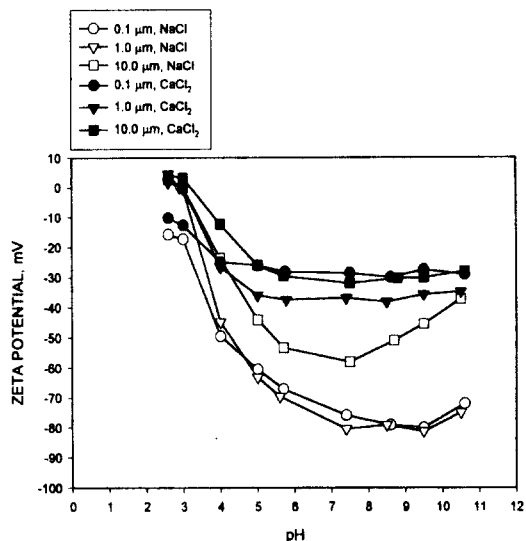The results show that the PZPC of latex particles occurs below a pH of 3.0. However, the 0.1μm

Fig. 2. Effects of pH on zeta potential for the latex particles. Constant electrolytes are NaCl of 10^{-3}M and CaCl$_2$ of 5×10^{-4}M.

particles revealed the increased negative ζ -potentials for pH values below 3.0. It is not possible to resolve the mechanism of this based on the experimental results of this study even though surface chemistry theory suggests that the smaller the particles, the easier they coagulate.

The manufacturer of the particles has stated that the three sizes of particles used in this study have the same weak acid surface group(carboxylic acid). This group has pK_a^{int} values(negative logarithm of the intrinsic acid dissociation constant) in the range of $4.0 \sim 5.0$. The degree of ionization of a surface carboxylate group depends on the pH of solution and increases with increasing pH. In Fig. 2, the results for the 0.1 μm and 1.0 μm particles at 10^{-3} M NaCl indicate that the maximum negative ζ -potentials are reached at a pH of 9.5. The decreasing negative ζ -potential after this pH indicates that all of the surface sites may have been deprotonated at a pH of 9.5. At this pH Na^- may be electrostatically attracted to a location inside of the plane of shear near the particle surface and may slightly compress the EDL(Hunter, 1981; Tobiason, 1987; Kim, 1993). The effect of pH on the interaction of calcium with the latex surface is somewhat surprising(see Fig. 2). As the pH increased from 5.0 to 10.5 the net number of ionized carboxylic acid surface sites(it gives a negative potential) was not expected to be altered significantly. Such is the reason why Ca^{2+} may be continuously and specifically adsorbed on, and may equally compensate the ionized surface sites generated as the pH increases. The effect of calcium on the ζ -potential is not affected by solution pH values above 5.0 at a concentration of 5×10^{-4} M $CaCl_2$.

The experimental results are average ζ -potentials of an aggregate of colloidal particles for each particle size. There are two ways to determine the average ζ -potentials using the LASER ZEE METER. One is the so-called high particle concentration measurement(the concentration is 10^6 to 10^9 particles/mL), which is the normal method for the measurement. That is, several ζ -potentials are measured and an average value is then calculated by hand. The other is the so-called low particle concentration measurement, which is the method by which an average is automatically computed by the machine from

measured values for individual particles for approximately 30 seconds. For 10.0 μm particles, the concentration of 4.55×10^5 particles/mL was used for the measurements and it was not enough for the normal method. Consequently, the low concentration measurement was utilized for the 10.0 μm latex particles and it resulted in a somewhat low negative ζ -potential at the solution of NaCl.

It has generally been assumed that oxide surfaces (glass/water interfaces) are truly amphoteric, where all surface hydroxyls have been considered capable of binding and releasing protons. On the basis of this assumption, oxide surface sites are usually modeled as diprotic acid groups(Dzombak and Morel, 1987; Hunter, 1981). However, the monofunctional surfaces such as carboxylated polystyrene latexes or ionizable monolayers have been generally assumed not to be amphoteric. With such monofunctional surfaces there is theoretically no IEP and no ζ -potential reversal(Hunter, 1981). Hunter(1981) has presented the pH effect for the electrophoretic mobility of three different latex particles with monofunctional surface group. The result was that in 1:1 electrolyte solution ζ -potential approaches zero asymptotically as the pH approaches zero. The manufacturer states that the latex particles used in this study have carboxylate surface groups. In the present study, however, the particle ζ -potential measured at 10^{-3} M NaCl changes from a negative to a positive value below about a pH of 3.0, that is, there exists a charge reversal below a pH of 3.0(see Fig. 2). This indicates that the particles may have other surface functional groups that have amphoteric or zwitterionic surface properties. James et al.(1978) suggested that in addition to monofunctional groups, latex particles may have more than one kind of functional group such as mixed sulfonate and carboxylate groups or as zwitterionic carboxylate and amine groups, depending on conditions of preparation. The interpretation of electrokinetic potentials of latex particles relates to uncertainties about the exact nature of the surface region of such particles. Hunter(1981; p. 267) suggested that "the surface structure of latex particles consists of flat hydrophobic regions with well-anchored(bound-in) functional groups; the whole surface region is assumed to be impermeable to water and to have little by way of dangling

or interwoven polymer chains. It is also assumed that there is no gel layer, nor is there any entrapment of excess emulsifier or initiator impurities. It must be admitted, however, that there is a possibility that some of the surface charge groups reside behind the physical surface, possibly associated with some buried water." Therefore, in this study the particles were assumed to be so-called amphoteric latex.

The values of ζ -potential for the latex particles as a function of the concentrations of Na$^-$ or Ca^{2-} at a pH of 5.7(unaltered DI water pH) are shown in Fig. 3. The different concentrations of sodium and calcium were prepared adding the desired amount of NaCl and CaCl$_2$. In general, the results show that the magnitude of the negative values of ζ -potential monotonically increased as the concentrations of Na$^+$ or Ca^{2+}([Na$^-$] or [Ca^{2+}]) decreased(the values of pNa or pCa increased). At the lowest calcium level(pCa = 5.3), the 0.1μm and 1.0μm particles had a relatively large negative ζ -potential of -62 mV. The magnitude of the negative values of ζ -potential increased $\sim$-8 mV to -15 mV as [Ca^{2+}] increased to 5×10^{-3} M (pCa = 2.3). This result is in contrast to the effect of pH variation for the constant calcium concentration (see Fig. 2).
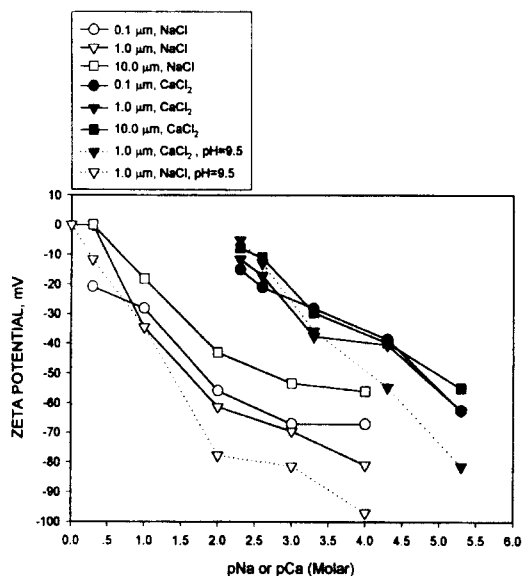
In Fig. 3, in the case of 1.0μm, the ζ -potential

reversal was not observed despite a sodium concentration of 1 M(pNa = 0.0). Here, the ζ -potential should approach zero(IEP) asymptotically as the pNa approaches zero. This result indicates that Na$^+$ does not interact in a specific chemical manner(specific adsorption) with the latex surface but has an electrostatic attraction into a fixed layer, the extent of which is affected by [Na$^+$]. This means that NaCl acted as an IDI for the latex particles with carboxylic acid surface groups.

In Fig. 3, in the case of calcium chloride electrolyte, ζ -potential reversal may be expected to occur around 3.16×10^{-2} M CaCl$_2$. The ζ -potential results indicate that Ca^{2-} interacts in some specific manner with the latex surface at a location inside of the plane of shear. The mechanism could be a specific chemical interaction (specific adsorption) with the carboxylate groups on the latex surface. Another possibility is that Ca^{2-} is electrostatically attracted in a fixed or Stern layer of ions adjacent to the surface. A determination of the mechanism of specific interaction is not possible based on the experimental results of this study.

When Ca^{2-} is adsorbed on the latex particles with carboxylate groups and Ψ_0 is constant, the EDL is compressed and PDI adsorption reactions are then facilitated and more PDIs are forced to adsorb at the surface in order to maintain a constant surface potential(Hunter, 1981). σ_β is then higher than it would be if no such specific effects were present. σ_0 then increases by induction. σ_0 is compensated for by the countercharge, σ_β, without any effect on σ_d. The overall electroneutrality ($\sigma_0 + \sigma_\beta + \sigma_d$) is zero and the negative values of both Ψ_β and Ψ_d (or ζ -potential) may diminish (Lyklema, 1982; Hunter, 1981; Stumm and Morgan, 1981). Generally, calcium is more effective at reducing the negative ζ -potential. In this study, H$^-$ and OH$^-$ acted as a PDI.

For 1.0μm particles, the magnitude of the negative values of ζ -potential at pH = 9.5 is larger than that at pH = 5.7 at the concentrations above pNa = 1.0 and pCa = 3.5 for each electrolyte(i.e., NaCl and CaCl$_2$), and the ζ -potential difference between these two pHs increases when the electrolyte concentration decreases above pNa = 1.0 or pCa = 3.5(see Fig. 3). When each electrolyte concen-

Fig. 3. Effects of electrolytes on zeta potential for the latex particles. A pH is 5.7.

tration increases below pNa = 1.0 or pCa = 3.5, the ζ-potential at pH = 9.5 is approximately the same as that at pH = 5.7. In other words, at any pH, as the electrolyte concentration increases, the ζ-potential at NaCl initially becomes less negative until it reaches zero whereupon it would no longer change with concentration, while the ζ-potential at CaCl$_2$ initially becomes less negative and would cross zero and then may become more and more positive until it reachs a maximum after which it will no longer change with concentration(see Fig. 3). It is interesting to note that the same electrolyte can make the value of ζ-potential for the particles change depending on its concentration and pH.

3.2. Collector Zeta Potential

The electrokinetic or ζ-potential of the glass beads collector can be measured using the streaming potential technique(Hunter, 1981). The streaming potential is the electric potential resulting from the flow of an electrolyte through a capillary, porous plug, or bed of granular material. The ζ-potential can be calculated from the data of the streaming potential using the Helmholtz-Smoluchowski equation(Eq. (1)). The values of ζ-potential are presented in Figs. 4 and 5. The results show that the ζ-potential of glass beads was controlled by pH and pNa and a PZPC might be found at a pH below 3.0. Parks(1965, 1967) has reported that the PZPC of SiO$_2$ is 2.2.

In Fig. 4, the ζ-potential systematically becomes more negative as the pH increases from 3.0 to 9.5. The results show that the negative ζ-potential roughly increased as pNa increased at a pH. Below 10^{-3} M NaCl the reduced negative ζ-potentials at a pH of 10.5 indicate that Na$^+$ may interact with the collector surface at a location inside of the plane of shear and may slightly compress the EDL. Na$^+$ does not interact in a specific chemical manner(specific adsorption) with the glass surface. Thus it is believed that Na$^+$ has an electrostatic attraction into the Stern layer, the extent of which is affected by [Na$^+$] (Hunter, 1981; Tobiason, 1987; Kim, 1993). It was also possible, as shown in Fig. 4, that the increasing pNa affected the location of the plane of shear and caused a lower ζ-potential to be measured. Hence, H$^+$ or OH$^-$ acted as a PDI at the glass/water interfaces
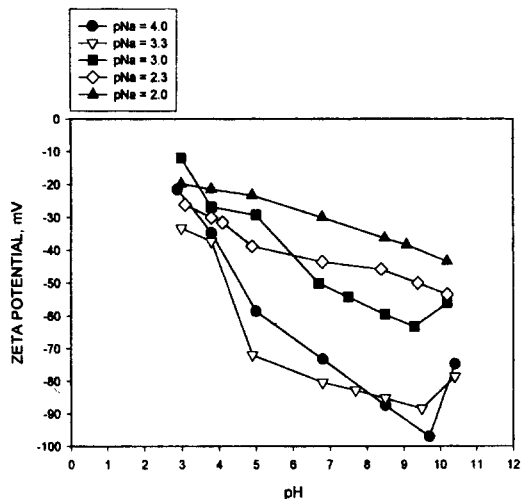

Fig. 4. Effects of different[Na$^+$] and pH on zeta potential for the glass beads collector. Different[Na$^+$] was maintained with NaCl.

while Na$^+$ acted as an IDI.

In Fig. 5, the results show that the ζ-potential was reduced as the ionic strength was increased but in each case was influenced little by pH values above 5.0. There also appeared to be a specific chemical interaction of calcium with the surface. The increase in the magnitude of ζ-potential is most pronounced between a pH of 3.0 and 5.0. A mechanism for this type of behavior can be proposed by following the same line of reasoning used in discussing the behavior of the latex particles. However, the effectiveness of a constant [Ca^{2-}], with the exception of the CaCl$_2$ of 2.5 × 10^{-5} M(pCa = 4.6), in reducing the ζ-potential, was limited as the pH was increased from 5.0 to 10.5. This was consistent with observed increases in Ca^{2-} adsorption on silica surfaces in this pH range (Tadros and Lyklema, 1969).

Generally, a silica surface is strongly hydrated in water and consists predominantly of silanol groups(>SiOH or >Si(OH)$_2$). The value of the ζ-potential reflects the effect of pH on the surface chemistry of a silica surface. As the pH increases, more of the surface silanol(>SiOH) groups are deprotonated(>SiO$^-$) and the surface charge becomes more negative. At pH values less than the PZPC, there are more positive sites(>SiOH$_2^-$) than negative sites and the charge becomes positive (eg., Schindler et al., 1976; Dzombak and Morel,
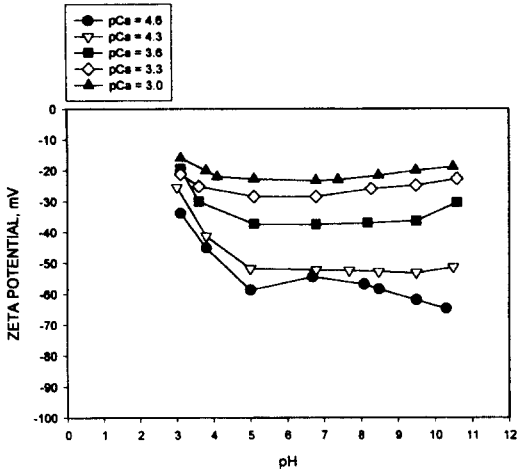
Fig. 5. Effects of different$[Ca^{2+}]$ and pH on zeta potential for the collector. Different$[Ca^{2+}]$ was maintained with $CaCl_2$.

1987). Surface silanol groups have ion exchange capacity. Increasing pH increases cation exchange capacity(CEC) while decreasing pH increases anion exchange capacity(AEC). Increasing $[Ca^{2-}]$ compresses the EDL and renders cation exchange more feasible(Drever, 1982).

With the cation exchange, the nature of the silica surface changes from one consisting of an array of strongly hydrated silanol groups to one presenting an assortment of both exchanged and unexchanged sites. As a rule, the conditions of pH and electrolyte concentration at which ion exchange begins depend primarily on the nature of the counterion. The higher the charge, the smaller the solvated volume, and the greater the polarizability of a cation, the more pronounced is its tendency to ion exchange(Allen and Matijević, 1969).

The ζ-potentials of different types of glass spheres have been measured using streaming potential(FitzPatrick, 1972; Gregory, 1964) and electro-osmosis (Kowlakowski and Matijević, 1979). Jednaćak and Pravdić(1974) employed the streaming current technique to measure ζ-potential for porous plugs made from crushed samples of quartz, vitreous silica and several types of glass. For crushed quartz, electrophoretic mobility(Li and De Bruyn, 1966) and streaming potential(Gaudin and Fuerstenau, 1955) results have also been published.

The results of other researchers obtained for chemical conditions similar to those of the present study, and collector ζ-potentials calculated from the streaming potential results of the present study, are presented in Fig. 6. This figure shows results for the effects of pH values of 3.0 to 10.5 on the ζ-potential in a 10^{-3} M monovalent electrolyte solution. The results show that a wide range in the ζ-potential has been measured for the types of surfaces considered. This may be caused by the different macroscopic properties of the various forms of silica. However, researchers have stated that their electrokinetic characteristics are, in general, similar(Iler, 1979; James and Parks, 1982).
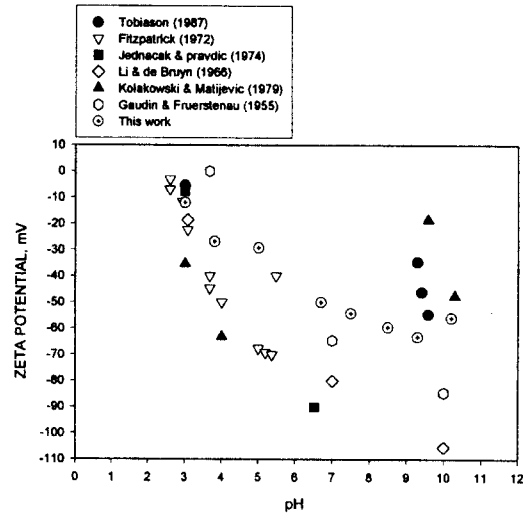

Fig. 6. Measured zeta potentials for various glass and silica in 10^{-3}M monovalent electrolyte for pH values from 3.0 to 10.5.

4. Conclusions

This study measured the ζ-potential of both latex colloidal particles with carboxylate surface group and glass beads with silanol surface group at various simple solution conditions(pH, $[Na^-]$, and $[Ca^{2-}]$). The results have been compared with the surface chemistry theory. Conclusions which may be drawn from the results of this study are presented below.

1. The negative ζ-potential values of the particle and collector rapidly decreased when the pH decreased below a pH of 5.0. This behavior was independent of the type of electrolyte solution.

These values steadily increased in a monovalent electrolyte(sodium chloride) solution when the pH increased from 5.0 to 9.5. However, little change in these values were observed in a divalent electrolyte(calcium chloride) solution in the same pH range. In other words, the more the pH decreases, the larger the effect of neutral salts such as NaCl and CaCl$_2$ have on the ζ -potential values.

2. The magnitude of the negative values of ζ -potential of the particle and collector monotonically increased as the concentrations of Na$^+$ or Ca^{2+}([Na$^+$] or [Ca^{2+}]) decreased(the values of pNa or pCa increased). In the case of latex particles, the ζ -potential should approach zero(IEP) asymptotically as the pNa approaches zero, while in the case of calcium chloride electrolyte, ζ -potential reversal may be expected to occur around 3.16×10^{-2} M CaCl$_2$(pCa = 1.5).

3. Sodium ion does not interact in a specific chemical manner(specific adsorption) with the particle and collector surfaces but has an electrostatic attraction into a fixed layer, the extent of which is affected by[Na$^+$]. This means that NaCl acted as an IDI for the latex particles with carboxylic acid surface groups and the glass beads collector with silanol surface groups.

4. Calcium ion interacts in some specific manner with the particle and collector surfaces at a location inside of the plane of shear. The mechanism could be a specific chemical interaction(specific adsorption) with the carboxylic acid surface groups on the particle and the silanol surface groups on the collector. Another possibility is that Ca^{2+} is electrostatically attracted in a fixed or Stern layer of ions adjacent to the surfaces.

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