EFFECT OF ALKALI METAL CATIONS ON
ADSORPTION OF GUAR GUM ONTO QUARTZ

by

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B.Sc., Northeastern University, 1996

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
MINING ENGINEERING

THE UNIVERSITY OF BRITISH COLUMBIA

April 2005

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Abstract

The effect of alkali metal chlorides (LiCl, NaCl, KCl, CsCl) on the adsorption of guar gum, a naturally occurring polysaccharide, onto quartz from dilute aqueous solutions of the electrolytes was investigated. The adsorption of guar gum onto quartz and the resulting colloidal stability of the system were determined through adsorption, zeta potential and turbidity measurements.

This thesis analyzes a previously undescribed phenomenon of enhanced polysaccharide adsorption in the presence of cesium and potassium cations. At the same time, lithium and sodium cations show no effect on the polysaccharide adsorption density compared to that observed in distilled water. These differences in the behavior of the simple alkali chlorides are attributed to their water structure breaking or water structure making capabilities. In this approach, since hydrogen bonding is the main adsorption mechanism, the polymer adsorption process is treated as a competition between polymer and water molecules for polar surface sites on the quartz surface. While water structure-breaking cations disturb the interfacial water layer allowing guar gum to more densely adsorb on the exposed surface silanol groups, structure-making cations better fit into the interfacial water layer and do not affect the guar gum-water competition for the polar surface sites.

The results strongly suggest that simple alkali metal chlorides are not totally indifferent, and even in dilute solutions their water-structure making/breaking capabilities should be taken into account to better understand the behavior of a model system such as quartz-guar gum.

The study is relevant to several industrial flotation processes where polysaccharides are used as selective depressants. This thesis should be a valuable contribution to our understanding of the mechanisms of polysaccharide adsorption on mineral surfaces.

TABLE OF CONTENTS

Abstract	ii
Table of Contents	iii
List of Figures	v
List of tables	vii
Acknowledgements	viii
Objectives	ix
CHAPTER 1 Introduction	1
1.1 Water Structure and Aqueous Solution	3
1.1.1 Ion-Water Interactions	3
1.1.2 Interfacial Water	8
1.2 Surface Chemistry of Quartz	10
1.2.1 General Information	10
1.2.2. Quartz-Water Interface	12
1.2.3 Surface Charge of Quartz	14
1.2.4 Electrical Double Layer Around a Charged Particle	16
1.3 Guar Gum	22
1.3.1 General Information	22
1.3.2 Hydration of Guar Gum	24
1.3.3 Adsorption of Polymers	26
CHAPTER 2 Experimental Procedures	30
2.1 Materials	30
2.2 Methods	35
2.2.1. Adsorption tests	35
2.2.2. Zeta Potential Measurements	36
2.2.3 Turbidity	38
CHAPTER 3 Results	39
3.1 Zeta Potential Measurements	39
3.2 Adsorption Measurements	44
3.3 Turbidity Measurements	50
CHAPTER 4 Discussion	53

CHAPTER 5 Conclusions.....	60
RECOMMENDATIONS.....	61
REFERENCES	62
APPENDICES	74
Appendix 1. Calibration Curve for Guar Gum	74
Appendix 2. Calibration Curve for Dextrin	74
Appendix 3. Calibration Curve for Dextran.	75
Appendix 4. Adsorption Isotherms for Dextran on Quartz.....	75
Appendix 5. Data of Adsorption Measurements.....	76

List of Figures

Figure 1.1.	A simple model for the water structure modifications produced by a small ion.....	4
Figure 1.2 .	Viscosity of alkali halide solutions as a function of concentration.....	6
Figure 1.3.	Functional groups that occur on the surfaces of quartz.....	10
Figure 1.4.	Surface densities of the functional groups on quartz as a function of pH.....	14
Figure 1.5.	A modern view of electrical double layer.....	16
Figure 1.6.	A structural formula of guar gum.....	22
Figure 1.7.	Swelling ratio of PVP gels in aqueous solutions of Chlorides.....	25
Figure 1.8.	Configuration of an adsorbed polymer molecule on a solid surface.....	26
Figure 2.1.	An X-ray diffraction pattern for the quartz sample.....	31
Figure 2.2.	The pore size distribution of the quartz sample.....	32
Figure 2.3.	Particle size distribution of the quartz sample.....	33
Figure 3.1.	Zeta potential of quartz in 0.01 M solutions of salts.....	39
Figure 3.2	Zeta potential of quartz in 0.1 M solutions of salts.....	40
Figure 3.3	Zeta potential of quartz in 0.01M CsCl, conditioned for 30 minutes and 24 hours.....	41
Figure 3.4	Zeta potential of quartz in 0.01M KCl, conditioned for 30 minutes and 24 hours.....	41
Figure 3.5	Zeta potential of quartz in 0.01M NaCl, conditioned for 30 minutes and 24 hours.....	42
Figure 3.6	Zeta potential of quartz in 0.01M LiCl, conditioned for 30 minutes and 24 hours.....	42

Figure 3.6	Zeta potential of quartz in 0.01M LiCl, conditioned for 30 minutes and 24 hours.....	42
Figure 3.7	The effect of guar gum addition on the zeta potential of quartz particles. Guar gum concentration 120 mg/L.....	43
Figure 3.8	Adsorption isotherms of guar gum on quartz at pH 5.2 and alkali metal chloride concentration of 0.01 M. A set of adsorption results for a dextrin sample is also included.....	44
Figure 3.9	Effect of ionic strength on the adsorption of guar gum at pH 5.2.....	45
Figure 3.10	Effect of pH on guar gum adsorption on quartz. pH adjustments were made with various hydroxides or with hydrochloric acid. Initial guar gum concentration 90 mg/L.....	46
Figure 3.11	Adsorption of guar gum as a function of pH in the presence of 0.01 M background electrolytes. Initial guar gum concentration 90 mg/L	47
Figure 3.12	Co-effect of background electrolyte and added base on the adsorption of guar gum. Initial guar gum concentration 90 mg/L.....	48
Figure 3.13	Co-effect of KCl and NaCl on the adsorption of guar gum at natural pH (5.2). Ionic strength 0.01 M. Initial guar gum concentration 120 mg/L.....	49
Figure 3.14	Effect of alkali metal cations on the stability of quartz	50
Figure 3.15	Turbidity of the guar gum-quartz system in the presence of 0.01N electrolytes at natural pH.....	51
Figure 3.16	Turbidity of the guar gum-quartz system in the presence of 0.01M electrolytes at pH 10.....	52
Figure 3.17	Turbidity of the guar gum-quartz system in the presence of 0.1M electrolytes at natural pH.....	52

List of Tables

Table 1	Free energies of hydration of hydrogen cation and alkali cations at 25 °C.....	7
Table 2	Crystallographic and hydrated radii for alkali metal cations.....	18

Acknowledgements

The work presented here was funded by:

Natural Sciences and Engineering Research Council of Canada.

The work was directed and supervised by:

Dr. Marek Pawlik

The advice and support of all is greatly acknowledged.

Objectives

1. To demonstrate the role of simple alkali metal cations in the adsorption of guar gum onto quartz
2. To show the effect of alkali metal ions on the flocculation/dispersion of quartz by guar gum.
3. To propose a mechanism of quartz-guar gum interactions in the presence of alkali metal cations.

CHAPTER 1 Introduction

The mode of action of natural and synthetic polysaccharides in the selective flotation of minerals has been a subject of very extensive research over the past 20 years. Starches, dextrans, various gums and synthetic derivatives of cellulose (e.g. carboxymethyl cellulose) have been tested as slime blinders, selective depressants of naturally hydrophobic minerals, and selective depressants of base metal sulfides.

There is only a limited number of successful industrial applications of these very environmentally friendly reagents. In potash flotation, a process that is carried out in a saturated KCl/NaCl brine, guar gum is routinely used to “blind” water insoluble slimes such as clays, carbonates and quartz. The role of guar gum is to adsorb on these sub-micron particles and prevent a cationic amine collector from adsorbing onto these unwanted particles.

In iron ore processing, hematite can be separated from quartz by a reverse flotation process in which starch selectively flocculates and blinds hematite allowing quartz to be floated using a cationic collector.

Certain sulfide ore operations use carboxymethyl cellulose to depress the floatability of naturally hydrophobic gangue minerals such as talc or graphite. In the flotation of platinum group metals-bearing ores guar gum is used to depress talc.

In the current industrial practice of sulfide ore flotation, the selective separation of bulk flotation concentrates is potentially a very important area of polysaccharide application since toxic depressants such as sodium bisulfide (NaHS) or cyanides are still standard reagents.

In all these processes, the use of polysaccharides is based on a “trial-and-error” approach rather than on a sound scientific evidence.

The common view that polysaccharides are non-selective (i.e. that they indiscriminately adsorb on all minerals), the general lack of understanding of the mechanisms involved in polysaccharide adsorption, and the fact that a wide chemical variety of these reagents exists strongly hinder their wider application.

As will be discussed, a number of different adsorption mechanisms were proposed in the literature even for the same mineral-polysaccharide system. As this thesis will show, a very important, previously undescribed phenomenon has systematically been overlooked in all the studies on polysaccharide adsorption. Simple alkali metal chlorides, very common salts in mineral processing systems, are routinely assumed to be indifferent, so-called background electrolytes towards mineral surfaces. The presented analysis of the results strongly indicates that adsorption data for a given mineral-polysaccharide system can be misinterpreted if the water structure-making or breaking properties of the alkali metal chlorides are not taken into account. This dissertation opens a whole new area for further research of polysaccharide-mineral interactions.

1.1 Water Structure and Aqueous Solution

Physicochemical methods of fine particle processing, e.g. flotation, flocculation, oil agglomeration, and even filtration, rely on interfacial phenomena occurring at the mineral-solution interface. Reagent adsorption, changes in the resulting wettability of minerals, or the state of fine particle aggregation/dispersion are just some of the underlying processes that have been researched in quite a detail. However, the main focus of all the past studies was on “the mineral surface”, or “the reagent”. Although the presence of water molecules at the mineral-solution interface is taken for granted, the role of the interfacial water and its structure have never been adequately correlated with mineral-reagent interactions.

1.1.1 Ion-Water Interactions

Liquid water has long been known to possess distinctive structural features, i.e. it retains a certain degree of similarity to ice. The amount of this “ice-likeness” may be altered by changes in temperature and pressure, and may also be affected by the presence of solutes (Frank and Wen, 1957). In particular, charged species strongly distort the structure of surrounding water, as a consequence of the change of microscopic balance of intermolecular forces, from that of water-water interactions in the pure solvent to ion-water interactions in the resulting solution (Chialvo et al., 1999).

Because ion-water interactions are determining factors in the behavior of aqueous solutions, with wide application in biological, geochemical, environmental and industrial processes, the structure of water and the effect of ions upon it have been a subject of numerous investigations. These studies were frequently based on the scheme introduced by Frank and Wen (1957), and Gurney (1953) who analyzed the behavior of ions in terms of their *water-structure breaking* and *water-structure making* capabilities. This model is schematically illustrated in Figure 1.1.

Figure 1.1 shows that an ion in aqueous solution is surrounded by three concentric regions. Region A is composed of immobilized water molecules, which are highly

ordered by the ionic field. In region B, the water molecules are less ordered. These water molecules are more random in organization than the ones in the water networks or water clusters in bulk water (note that bulk water is composed of free water molecules and water networks or water clusters whose component water molecules cannot move as freely as free water molecules). Region C represents bulk water.

Figure 1.1. A simple model for the water structure modifications produced by a small ion (Frank and Wen, 1957).

Region A: immobilized water molecules (hydration sheath);

Region B: less ordered water molecules (region of structure breaking);

Region C: bulk water.

In region A, water molecules are tightly bound to the ion. Region B extends farther away from the ion and is referred to as the region of structure breaking. Only at larger distances, where the ionic field is weak, water molecules form the “normal” ice-like structure. Small (in terms of crystallographic radii), strongly hydrated ions reinforce the “normal” structure of water and the region of structure breaking (region B) disappears. In contrast, large poorly hydrated ions disturb the ice-like structure and generate an extensive region of structure breaking so that region A disappears. Structure-breaking ions are also referred to as chaotropes whereas structure-makers are known as kosmotropes (De Xammar Oro, 2001).

Experimentally, these two effects can readily be distinguished through viscosity measurements. Increasing concentrations of structure-breaking ions result in a decrease of the viscosity of aqueous solutions. On the other hand, increasing amounts of structure-makers significantly increase the viscosity of water (Stokes and Mills, 1965). In general, the variation of the relative viscosity η_r with the molarity c can be represented by Jones and Dole equation:

$$\eta_r = \eta / \eta_0 = 1 + A_\eta c^{1/2} + B_\eta c \quad (1)$$

where η and η_0 are the viscosities of the solution and solvent respectively, A_η is a constant depending on the long-range coulombic forces, and B_η is an adjustable parameter which is related to the size of the ions and to different ion-solvent interactions.

The Jones and Dole equation is limited to fairly low concentrations (< 0.1 M). For higher concentrations, additional parameters are required. In most cases, it is sufficient to add a second order term, c^2 (Kaminsky, 1957):

$$\eta_r = \eta / \eta_0 = 1 + A_\eta c^{1/2} + B_\eta c + D_\eta c^2 \quad (2)$$

The viscosity B_η coefficient provides a very useful quantitative measure of ions' effects on water structure (Gurney, 1953). For structure breaking ions, the viscosity B_η coefficients are negative, while structure making ions give positive B_η coefficients.

Figure 1.2 shows the relative viscosity versus concentration for aqueous solutions of halide salts. All the curves follow the parabolic equation 2. It is clear from Figure 1.2 that increasing concentrations of LiCl and NaCl result in relative viscosities greater than 1, while the remaining alkali halides (KCl and CsCl) continuously decrease relative viscosities. On this basis, Li^+ and Na^+ are classified as structure making ions while K^+ and Cs^+ are classified as structure breaking ions.

Figure 1.2. Viscosity of alkali halide solutions as a function of concentration. (Weast, 1971).

It is also important to point out that the free energies of hydration of alkali metal cations vary greatly from Li^+ to Cs^+ . A selection of so-called “best” single-ion data is given in Table 1 (Franks, 1972). The free energies of hydration also show that the

hydration of Li^+ is more thermodynamically favorable than the hydration of Cs^+ . This ordering of ions from the least to the most hydrated is known as the Hofmeister series (Napper, 1970).

Table 1

Free energies of hydration of hydrogen cation and alkali metal cations at 25 °C

Ions	H^+	Li^+	Na^+	K^+	Cs^+
Free energies of hydration [kcal/mol]	- 260.5	- 123.5	- 98.3	- 80.8	- 71

1.1.2 Interfacial Water

Water molecules tend to adsorb on all surfaces, especially on polar surface sites. Most insoluble metal oxides (if not all) adsorb water by chemisorption to form surface hydroxyl groups on top of which water molecules are physically adsorbed. The two species, surface hydroxyl groups and adsorbed water molecules, can readily be identified by infrared spectroscopy (Little, 1966).

There is considerable evidence that liquid water becomes highly structured as some types of surfaces are approached. If the solid surface is *crystalline* and the surface atoms are in an orderly arrangement, e.g. quartz, one can imagine an orderly arrangement of adsorbed water molecules which, through hydrogen bonding, could cause an extension of such an order (ice-like structure) for some distance into the solution, producing a network of water molecules (Drost-Hansen, 1977). However, such ordered structuring of water is highly unlikely to occur on the surface of *amorphous* silica, on which the SiOH groups have no regularity beyond two or three silanol sites (Iler, 1979).

The interfacial water structure is fundamentally different in nature from the normal structure of the clusters in bulk water:

1. The interfacial structure is more stable with respect to temperature and hydrostatic pressure than the bulk structure (Horne et al, 1968). For example, interfacial water remains "liquid" down to about -40°C (Schufle and Venugopalan, 1967).
2. Compared with bulk water, the interfacial water has a higher viscosity (Henniker, 1949).
3. Ion transport processes such as diffusion and electrical conductivity are roughly 10 times slower in interfacial water than in bulk water (Spiegler and Coryell, 1953; Richman and Thomas, 1956).
4. The interfacial water has a lower vapor pressure (Franks, 1972).
5. The interfacial water has a higher specific gravity (Franks, 1972).

It is quite certain that the properties of the interfacial water mentioned above are determined by interactions with the surface. The SiOH groups are stationary and are often ordered into patterns which might fit into the ice structure. Within a thin film or pore, the dimension of the film or pore may affect water structure by not allowing sufficient space for the development of bulk water structure (Franks, 1972).

1.2 Surface Chemistry of Quartz

1.2.1 General Information

Quartz is the main gangue mineral in practically every flotation separation. A significant proportion of the available literature concerning polymer adsorption at the solid–aqueous solution interface concerns quartz (Trompette et al., 1994; Bohmer and Koopal, 1992). Consequently, the chemistry associated with quartz surfaces has been widely studied, as summarized in comprehensive reviews by Bolt (1957), Iler (1979) and Bergna (1994). It should be noted that some features described here for quartz are derived from silica. Although the differences between amorphous silica and crystal quartz are obvious, they do have numerous common surface properties and hence are considered similar by some researchers (Kisielew, 1970; Staszczuk, 1985).

The surface properties of quartz are determined by the presence of functional groups on the surfaces of quartz. In general, several different functional groups can be found on the surface of quartz, depending on the preparation or origin of the mineral and, if in solution, the nature of that solution. Functional groups commonly associated with the quartz surface are depicted schematically in Figure 1.3.

Figure 1.3. Functional groups that occur on the surfaces of quartz (Bergna et al., 1994).

When surface chemical groups are mainly siloxane Si-O-Si groups, the surfaces of quartz are hydrophobic; when the surfaces expose silanol Si-OH groups, they are hydrophilic (Iler, 1979). Hydrophobic quartz can reversibly be rendered hydrophilic by hydroxylating the siloxane Si-O-Si groups into silanol Si-OH groups (Lamb and Furlong, 1982).

1.2.2. Quartz-Water Interface

When quartz is exposed to water, it reacts to form surface silanol groups (Si_sOH) (Iler, 1979):

The silanol groups are commonly believed to be the sites for adsorption of water molecules (Iler, 1979). In a detailed study of the behavior of water on the surfaces of quartz, Klier and Zettlemoyer (1977) showed that water molecules sit “oxygen down” on the SiOH groups. Michelle et al. (1990) observed that decreasing the number of surface silanol groups by dehydroxylation led to reduced adsorption of water on the surfaces of quartz.

The water film on the surfaces of quartz is strongly bonded to quartz and hence possesses properties different from those of bulk water (Staszczuk, 1985). There is evidence from viscosity measurements that a monolayer of water molecules is immobilized on the SiOH surface by hydrogen bonding (Iler, 1979). Furthermore, Yalamanchili et al. (1995) detected an ordered ice-like interfacial water structure on hydrophilic silicon surface by in-situ Fourier transform infrared/internal reflection spectroscopy, and such an ordered ice-like interfacial water structure is believed to exist on all the surfaces of hydrophilic minerals. Iler (1979) also reported that the first two layers of water molecules on the surfaces of quartz possess quite a high viscosity and further deduced that the viscosity is probably shear-sensitive because of breaking of the hydrogen bonds between the first layer of water molecules and silanol groups.

As the temperature is raised, the hydrated water is removed and the hydroxyl groups condense to form siloxane bonds, evolving water (Iler, 1979):

Michelle et al. (1990) reported that on dry quartz surface's silanol groups start to condense and evolve water extensively above 170 °C. At 500 °C, approximately half of the silanol groups are removed. But, in this stage, most of the remaining hydroxyl groups are still in the neighborhood of another hydroxyl group. Above 750 °C, only isolated silanol groups remain. At 1000 °C, only 0.4 OH groups/Å² remain on the surfaces of quartz, compared to 4.6 OH groups/Å² for the fully hydroxylated quartz surface (Bergna et al., 1994). However, when dehydroxylated quartz is treated with water, surface OH groups can form again as a result of rehydroxylation (Zhuravlev, 2000).

1.2.3 Surface Charge of Quartz

Just like other mineral oxide surfaces, quartz has a surface charge character that is defined by the relative concentrations of H^+ and OH^- (the potential determining ions) in solution, as given by the following equations.

While SiO^- groups are responsible for the negative charge of quartz, $SiOH_2^+$ groups render quartz positively charged. Therefore, it is the relative magnitude of the equilibrium constants K_1 and K_2 in equations (1) and (2) that determine the net charge on the quartz surface. The pK values proposed in the literature (Hiemstra et al., 1989) are in the following ranges: $pK_1 = 3.0 \pm 1.0$ and $pK_2 = 7.0 \pm 1.0$.

Duval et al. (2002) reported the densities of the main functional groups on quartz as a function of pH (Figure 1.4).

Figure 1.4. Surface densities of the functional groups on quartz as a function of pH. (Duval et al. 2002).

It is generally accepted that the point of zero charge (pzc) for quartz occurs at approximately pH 2 (Bolt, 1957), and is somewhat dependent on the exact nature of the surface. Fig. 1.4 demonstrates that, at pH 2, the density of SiO^- groups is equal to that of SiOH_2^+ groups, thus defining the point of zero charge (pzc) of quartz. At pH values higher than the pzc, the density of SiO^- groups is higher than the density of SiOH_2^+ groups, rendering quartz negatively charged. In contrast, at pH values lower than the pzc, the density of SiO^- groups is lower than the density of SiOH_2^+ groups, resulting in positively charged quartz surfaces. Practically, all industrial flotation separations are carried out at neutral or alkaline pH values. In these systems, the quartz surface therefore is negatively charged.

When analyzing the quartz surface charge, the structure of the oxide layer is never a negligible factor. Hydroxylated quartz has a high density of hydroxyl groups that are in close proximity to one another (Bolt, 1957). It is also generally believed that adjacent groups (vicinal) can interact with each other through hydrogen bonding. Consequently, the hydroxyl hydrogen atoms are strongly bound at normal pH levels, resulting in the low surface charge of hydroxylated quartz.

1.2.4 Electrical Double Layer Around a Charged Particle

The ion concentration profile that develops around a charged particle in an electrolyte solution is commonly referred to as the electrical double layer (EDL). The layer of counter-ions close to the particle surface is usually strongly bound by electrostatic forces and as such is called “the inner layer” or “the compact layer”. Ions farther away from the surface are weakly attracted to the particle surface and these loosely attached ions form “the diffuse layer” (Figure 1.5).

Figure 1.5. A modern view of the electrical double layer (Bockris and Reddy, 1998).

The compact (inner) layer is divided further into the Inner Helmholtz Plane (IHP) and the Outer Helmholtz Plane (OHP). The IHP runs through the centers of specifically adsorbed ions, while the OHP runs through the centers of hydrated counter-ions at the distance of closest possible approach to the surface. The diffuse layer lies beyond the OHP.

When two charged particles randomly move in an electrolyte solution, the diffuse layer of EDL consisting of weakly attached ions is sheared off and the compact layer becomes exposed to other approaching or colliding particles. Due to this shearing effect, the compact layer is said to end at *the shear plane*, essentially where the OHP ends. By definition, the electrical work needed to bring a unit charge from infinity to the shear plane is referred to as *the zeta potential*. As such, the zeta potential can be viewed as the effective energy barrier that a charged particle senses as it approaches another charged particle (Hunter, 1993).

Adsorption of metal ions at mineral–water interfaces is a complex process involving many possible variables. Certain types of ions affect the surface charge by reacting with surface functional groups. Such ions are referred to as potential determining ions (PDI). The surfaces of oxide minerals possess hydroxyl groups due to strong hydration. These groups react with acids or bases to produce positive or negative sites (e.g. reaction 3 and 4 for quartz). Therefore, for oxide minerals, H^+ and OH^- ions are *potential determining ions*.

Ions that are not potential determining but are capable of strongly interfering the adsorption of PDI are called *specifically adsorbing ions*. These ions often show a strong chemical affinity towards the mineral surface.

However, there is no clear rule as to which kind of metal ions are permitted to move into the specifically adsorbed layer. Polyvalent and divalent ions have been reported to be capable of specific adsorption. Alkali metal salts (chlorides, nitrates, perchlorates) are normally treated as *indifferent electrolytes* towards mineral surfaces.

This means that the adsorption of alkali metal cations (counterions) on negatively charged mineral surfaces takes place only through electrostatic attraction without forming any permanent chemical bonds with the negative surface sites. Thus, the negatively charged surface sites are not neutralized by the cations, but are only partially screened. The extent of screening, which is also a function of electrolyte concentration, affects the measured zeta potentials. The higher the concentration of the indifferent electrolyte, the more efficient the screening of the surface charges and the lower the zeta potentials. This effect is also known as the compression of the electrical double layer (Hunter, 1993).

Iler (1979) and Bockris and Reddy (1998) summarized the development of the theories on the adsorption of metal ions onto quartz:

It was first recognized that metal ions, attracted by the negative charge of quartz, are kept in motion near the surface of quartz by thermal energy. Then it was realized that large ions cannot approach the surface of quartz as closely as small ions can. Note that after hydration, large ions, such as potassium and cesium, become smaller, while small ions, such as sodium and lithium ions, become larger (Table 2).

Table 2

Crystallographic and hydrated radii for alkali metal cations
(Robinson, 1959; Shannon and Prewitt, 1969)

	Li^+	Na^+	K^+	Cs^+
Crystallographic radii (Å)	0.74	1.02	1.38	1.70
Hydrated radii (Å)	2.37	1.83	1.38	1.70

Although the exact hydration number for cesium and potassium ions is not known, the hydrated and crystallographic radii of the ions are assumed to be equal since the hydration of these ions is very poor.

Other models of the electrical double layer have also been developed to model the adsorption of ions onto oxides, for example the site-binding model (Yates et al., 1974) and the tripple layer model (Davis et al., 1978; Hayes et al., 1987, 1988). Based on the tripple layer model, Sverienksy (2001) predicted the distances of adsorbed alkali ions from the surface of quartz. Sverienksy (2001) argued that for alkali ions to directly adsorb on the surfaces of minerals i.e. to enter the inner layer, they must lose their hydration water. Thus the calculated distance of closest approach correlated well with the hydrated radii of alkali metal ions.

The affinity of ions with different degrees of hydration towards oxide surfaces can be explained by a thermodynamic model of ion adsorption at the oxide-solution interface developed by James and Healy (1972). These authors made a clear distinction between the adsorption behavior of oxides characterized by a low dielectric constant and those characterized by a high dielectric constant. The model demonstrated that a low-dielectric oxide surface, such as quartz ($\epsilon = 4.6$), will preferentially interact with less hydrated cations while strongly hydrated cations will not as easily adsorb on such a surface. The opposite was predicted for titania, an oxide characterized by a dielectric constant of 120. These differences were attributed to the ease or difficulty for a metal ion to exchange its secondary hydration sheath for the interfacial water molecules upon approaching to the surface (adsorption was assumed to take place in the Inner Helmholtz Plane of the double layer). The structure of the interfacial water, as judged from the calculated values of the dielectric constant for these immobilized water molecules, was also an important factor.

Generally, for a series of ions with fixed charge, this solvation energy barrier for adsorption decreases as the crystallographic ionic size increases. The crystallographic

radii of alkali metal cations, and thus their affinity towards the quartz surfaces, increase in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$, but their hydrated radii increase in the opposite direction.

The ion adsorption sequences can also be explained by the “like adsorb like” concept (Dumont et al., 1990). According to this approach, surfaces with a high heat of immersion preferentially adsorb well-hydrated ions while surfaces with a low heat of immersion preferentially adsorb poorly hydrated ions. The degree of hydration of mineral surfaces is related to its heat of immersion and thus to the pzc of the mineral (Healy and Fuerstenau, 1965). Accordingly, high-pzc minerals preferentially adsorb well-hydrated ions and low-pzc minerals (e.g. quartz, pzc at $\text{pH} \approx 2$) preferentially adsorb poorly hydrated ions. This concept satisfactorily explains the observed adsorption sequences on quartz and a number of other oxides (Dumont et al., 1990).

Bockris and Reddy (1998) also stated that for alkali metal cations to enter the inner layer, the metal cations should be dehydrated, but only partial dehydration is required. They argued that, since small alkali metal cations tightly adsorb a large number of water molecules, these metal cations cannot easily get rid of their hydration sheath and thus will not enter the inner layer. On the contrary, large metal cations can only loosely adsorb much fewer water molecules. Such metal cations can easily throw away their hydration sheath and hence tend to enter the inner layer. For the alkali metal cations to enter the inner layer, some of the water molecules immobilized on mineral surfaces should be removed to make room for the alkali metal cations to adsorb.

This modern view of the electrical double layer clearly recognizes the presence of differently oriented water molecules at the interface. Bockris and Reddy (1998) and Bockris and Khan (1993) concluded that the water molecules in the inner-Helmholtz plane (IHP) are completely immobilized and strongly oriented, whereas water molecules in the outer Helmholtz plane (OHP) are only weakly oriented. According to, Drost-Hansen (1977) the immobilized water molecules on solid surfaces are capable of

producing a network of water molecules or water clusters through hydrogen bonding for some distance into the solution.

1.3 Guar Gum

1.3.1 General Information

Guar gum is a natural nonionic polysaccharide, obtained from the seeds of two annual leguminous plants, *Cyamopsis tetragonalobus* and *psoraloides*. Since its commercial introduction in 1953, the consumption of guar gum has grown rapidly. The rapid growth is largely because of guar gum's function not only in the traditional role of a viscosity builder for water systems, but also as a hydrogen-bonding, reagent-type chemical for such industries as mining and paper making (Maier et al., 1993).

Figure 1.6 shows a schematic depiction of the structure of a guar gum monomer.

Figure 1.6. A structural formula of guar gum.

Guaran, the functional polysaccharide in guar gum is a chain of (1→4)-linked β -D-mannopyranose units with α -D-galactopyranose units connected to the mannose backbone through (1→6) glycosidic linkages. The poly-mannose chain is randomly substituted with galactose units at a mannose-to-galactose ratio of 1.8-1.0 (Whistler and Hymowitz, 1979; Painter et al., 1979). The least substituted sections of the guar gum molecules show the greatest tendency to associate and precipitate, facilitated by the *cis*-

configuration of the mannose OH groups, while the more densely substituted regions serve to solubilize the precipitated gel-like structure (Dea, 1993).

Guar gum's unusually high ability to increase the viscosity of aqueous solutions is due to its large hydrodynamic volume and the nature of its specific intermolecular interactions (entanglements) (Maier et al., 1993). Like most high-molecular-weight polymers, guar gum shows pseudoplastic or shear thinning behavior in solution. The degree of pseudoplasticity of a guar gum solution increases with concentration and molecular weight. Solutions of guar gum do not exhibit yield stress properties (Bilgen, 1972).

Guar gum is stable over a wide pH range. In solutions of pH 3 or less, guar gum is hydrolyzed by acids, resulting in rapid loss of viscosity. Above pH 11, hydration of guar gum is depressed and low viscosity results. In industries, guar gum is still used where high pH conditions could hydrolyze synthetic polyamides, such as in hydrometallurgical leaching of aluminum from bauxite, soda from trona, and uranium from its ores. Thermal degradation occurs when guar gum solution is heated to 80 to 95 °C for extended periods of time, resulting in loss of viscosity (Goldstein and Alter, 1959; Maier et al., 1993).

1.3.2 Hydration of Guar Gum

A factor that has received little attention is the effect of hydration of a polymer on its adsorption properties. Ishihara et al. (1998) found that protein adsorption is reduced on highly hydrated substrates, while Haigh et al. (2000) showed a clear trend of increasing adsorption of IgG (immunoglobulin-G, an important blood protein) onto hydrogel surfaces with decreasing hydration. These phenomena have been attributed to the layers of water sterically inhibiting the adsorption of protein or IgG onto bio-substrates, which should also be an important aspect of interactions between polymers and mineral surfaces.

Most polymers influence the mobility and structuring of water beyond the immediate interface to a thickness of several molecular diameters (Blanshard, 1970; Barfod, 1988; Rickayzen, 1989). Yakubu et al. (1990) identified four forms of water on corn starch: tightly bound water, weakly bound water, surface trapped water and bulk water.

Okazaki et al. (1996) proposed the following mechanism for hydration of polymers:

1. Hydration of polymers is dominated by hydration to the hydroxyl group.
2. The hydration to the hydroxyl group is characterized as hydrogen bonding between the lone-pair electron on oxygen of the hydroxyl group and the proton of water.
3. The stability of hydrogen-bonding hydration is dependent on the electron-pair donation (EPD) and acceptance (EPA) abilities of water molecules.
4. These properties are enhanced or reduced via hydration to ions.

Takano et al (1998) measured the swelling ratios of PVP gels (poly *N*-vinyl-2-pyrrolidone), with a molecular weight of 6.3×10^5 , in aqueous solutions of chlorides (Figure 1.7).

Figure 1.7. Swelling ratio of PVP gels in aqueous solutions of chlorides. (Takano et al. 1998).

The swelling ratios were estimated as $(d/d_0)^3$, where d_0 is the diameter of the water-swollen gel and d is that of the salt solution-swollen gel. Figure 1.7 clearly demonstrates the effect of structure makers and breakers on the hydration of PVP gels. In the presence of Li^+ , a structure maker, the diameters of PVP gels increase because of a thicker water layer on the gel surfaces; while in the presence of K^+ and Cs^+ , structure breakers, the diameters of PVP gels decrease due to a thinner water layer on the surfaces of PVP gels.

Goldstein and Alter (1959) studied the effect of AlCl_3 , CaCl_2 and NaCl on the hydration of guar gum. The structure making capabilities of the cations increase according to the sequence $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Na}^+$. It was found that at electrolyte concentrations higher than 10% (by weight), the viscosities of guar gum solutions increased dramatically following the same sequence, with AlCl_3 producing the highest viscosity. This trend coincides well with the observations of Takano et al (1998) (Figure 1.7), i.e. when the concentration of an electrolyte is high enough, the effect of metal ions on the hydration of polymers becomes significant and depends on the structure making/breaking capabilities of the ions.

1.3.3 Adsorption of Polymers

The adsorption behavior of long chain polymers (flocculants) is quite complex and not well understood. There are many theories of polymer adsorption, as reviewed by Fler and Scheutjens (1993) but, generally speaking, it is accepted that a polymer molecule adsorbs simultaneously onto many sites on a solid surface assuming conformations referred to as trains, loops and tails as shown in Figure 1.8.

Figure 1.8. Configuration of an adsorbed polymer molecule on a solid surface.

The actual attachment to the solid surface can take place through many different interactions (Gregory 1987):

- *ionic (electrostatic) interaction*, when an adsorbate adsorbs on a surface bearing oppositely charged ionic groups, e.g. anionic caboxymethyl-cellulose on positively charged oxide surfaces.
- *hydrophobic bonding*, responsible for adsorption of nonpolar segments of polymers and surfactants on hydrophobic surfaces, e.g. aliphatic side chains of cellulose ethers on hydrophobic coals.
- *hydrogen bonding* takes place when the surface and the polymer have suitable H-bonding sites e.g. hydroxyl groups of polysaccharides and oxide minerals.
- *ion binding*, sometimes it is found that a certain amount of divalent metal ions (such as Ca^{2+} or Mg^{2+}) is required to promote adsorption of anionic polyelectrolytes onto negatively charged surfaces. These metal ions are known to bind strongly to

carboxylate groups and serve as links between these groups and negative sites on the surface. This mechanism is involved in the adsorption of anionic polymers (polyacrylates) on calcium-activated quartz surface.

- *dipole-crystal-field effects*, this mechanism is common in adsorption of polymers onto a crystalline salt-type surface, e.g. flocculation of minerals such as apatite and fluorite by polyacrylamide.

Practically all of the above mechanisms were proposed to explain interactions between polysaccharides and mineral surfaces. While **hydrogen bonding** was considered as the primary adsorption mechanism for starch (Balaji and Iwasaki, 1969; Hanna, 1973; Afenya, 1982), **hydrophobic bonding** was proposed for the adsorption of dextrin onto inherently hydrophobic minerals, such as talc, molybdenite and bituminous coal. (Wie and Fuerstenau, 1974; Haung et al., 1978; Miller et al., 1984). This was later apparently confirmed by experiments with oxidized coal (Miller et al., 1983). In the case of oxidized, hydrophilic coals, dextrin adsorption was substantially lower than on hydrophobic, demineralized ones. Evidence for **chemical interaction** of starch with calcite and hematite was also reported (Somasundaran, 1969; Khosla et al., 1984). The findings of Subramanian and Laskowski (1993) also indicate that dextrin adsorption on hydrophobic graphite, another hydrophobic model mineral, is associated with chemical interactions of dextrin with metal impurities rather than with hydrophobic bonding since the adsorption density decreased substantially after leaching trace metals off the naturally hydrophobic graphite surface.

The importance of **metallic sites** was demonstrated quite convincingly by Liu and Laskowski (1989). It was reported that while dextrin did not adsorb onto either hydrophilic quartz or methylated hydrophobic quartz, it adsorbed strongly onto both these samples when the quartz surface was activated with lead ions. Based on such results, Liu et al. (2000) generalized that all polysaccharides adsorb on mineral surfaces through complexation with metal-hydroxyl surface sites, and the nature of the interaction, whether hydrogen bonding or chemical, is of acid-base type and strongly depends on the acidity of the surface metal-hydroxyl groups. This postulate was consistent with the

observation that the adsorption of guar gum onto talc was strongly dependent on the surface concentration of magnesium sites (Rath et al., 1995; Rath et al., 1997).

In the case of guar gum, Whistler (1973) reported that the straight chain configuration of the molecule with its regularly occurring D-galactopyranosyl branches makes it well suited to form hydrogen bonds with mineral surfaces. Wang et al (2005) observed a substantial decrease in guar gum adsorption onto talc in the presence of urea, a hydrogen bond breaker. Based on this observation, and due to the fact that guar gum adsorption was not affected by ionic strength (adjusted with KCl), Wang et al concluded that hydrogen bonding was the main driving force behind guar gum adsorption onto talc. In a comparative study of guar gum and dextrin, Rath et al. (1997) reported higher adsorption density of guar gum onto talc than that of dextrin. This phenomenon was attributed to the more favorable cis-configuration of the hydroxyl groups in mannose, as opposed to the trans-configuration in dextrin, apart from the differences in their molecular weights. In contrast, Steenberg and Harris (1984) and Jenkins and Ralston (1998) proposed that the adsorption of guar gum on talc occurs mainly at the basal planes via **hydrophobic force**.

Rath and Subramanian (1997) proposed that the adsorption mechanism of guar gum on mica is governed by **hydrogen bonding** and **chemical interaction**. They also reported that adsorption densities of guar gum onto mica increase with pH (adjusted with KOH).

Pawlik et al. (2003) reported that the amount of guar gum adsorbed on illite, a typical potash ore component, was independent of ionic strength over a wide range of salt concentrations. The adsorption density of the polysaccharide on illite did not measurably change with ionic strength from that of distilled water to about 50%-saturated KCl/NaCl potash brine (~3M KCl/NaCl). However, guar gum adsorption on dolomite dramatically decreased over the same range of ionic strengths, and no reliable explanation of that phenomenon was proposed.

Adsorption of polymers affects the stability of fine particles towards aggregation. High molecular weight polymers can cause particle aggregation, the so-called “bridging flocculation”, by simultaneously adsorbing on several particles. When two particles coated with polymers are brought together it is possible for the loops and tails (Figure 1.8) of one polymer molecule to adsorb onto bare patches on the other particle and form “bridges”. However, when adsorption densities are so high that the adsorbed polymers cannot find available adsorption sites on another particle, the effectiveness of flocculants drops dramatically resulting in steric stabilization (Napper, 1970, 1977). The densely adsorbed polymer molecules provide a mechanical barrier that prevents particles from aggregating. This interparticle “repulsion” can be considered to arise from a swelling pressure at the point of sufficiently close approach (Kitchener, 1972). Therefore, depending on the dosage, even the same polymer can induce two opposite effects: flocculation or dispersion (steric stabilization).

CHAPTER 2 Experimental Procedures

2.1 Materials

Natural guar gum, Rantec KP4000, was obtained from Rantec Corporation. In Canada, Rantec KP4000 is widely used by the potash industry as a slime blinder. Guar gum has one of the highest molecular weights of all naturally occurring water-soluble polymers. Cheng et al. (2002) found that the molecular weight of natural guar gum is 1.935×10^6 , while Robinson et al. (1982) reported that the molecular weight of five commercial guar gums ranged from 4.4×10^5 to 16.5×10^5 . The molecular weight of KP4000 was calculated to be 1.39×10^6 by Pawlik and Laskowski (2004) based on their viscosity data using the following formula (Robinson et al., 1982):

$$[\eta] = 3.8 \times 10^{-4} M^{0.723}$$

Where $[\eta]$ is the intrinsic viscosity and M is the molecular weight.

As natural guar gum contains some insoluble residue, the following method was used to purify guar gum stock solutions and determine the percentage of the insoluble organics. First, a 100 ppm solution of raw guar gum was centrifuged at 10000g over various periods of time. Then the phenol-sulfuric acid method developed by Dubois et al (1956) was used to measure the absorbance of the guar gum solutions before and after centrifuging (see section 2.2.1 for the analytical details). It was found that the absorbance values did not change further after a centrifuging time of 30 minutes. The absorbance of the “raw” solution was 1.4711 and it decreased to 1.2957 after centrifuging. Therefore, a correction factor of 0.8808 ($1.2957 / 1.4711 = 0.8808$) was applied to obtain the actual guar gum concentrations. The correction factor indicates that the KP4000 sample contains about 12% of water-insoluble residue, which agrees well with previously published data for natural guar gums (Chatterji and Borchardt, 1981).

A stock solution of guar gum (1g/L) was prepared every other day by quickly adding 0.5 g of guar gum powder into 500 ml of vigorously stirred water and mixing for 4 hours to ensure complete hydration and dissolution of guar gum. Such a prolonged

dissolution procedure is also practiced by various operations utilizing guar gum. The stock solution was then centrifuged at 10000g for 30 minutes to remove any undissolved impurities.

A limited number of adsorption tests was performed with the use of dextrin (Tapioca Dextrin 12, from A.E. Staley, MW=56,000). Dextrin adsorption experiments were carried out for reference in distilled water, in 0.01M KCl and NaCl, and in 0.1M KCl and NaCl solutions. Dextrin was completely soluble in water and was used "as received".

A quartz sample for this study was obtained from Sigma-Aldrich. The sample was described by the supplier as "silicon dioxide, finely ground, naturally occurring microcrystalline silica, historically called amorphous". An x-ray analysis of this material confirmed that the sample is actually quartz and the positions of the observed diffraction

Figure 2.1. An X-ray diffraction pattern for the quartz sample.

peaks match perfectly the diffraction data for a standard quartz sample (“Selected Powder Diffraction Data for Minerals”, 1974). An x-ray diffractogram for the Sigma-Aldrich quartz is shown in Figure 2.1.

The BET (Brunauer Emmett Teller) specific surface area for the sample, determined from nitrogen adsorption after outgassing at 200⁰C under vacuum, was found to be 6.0 m²/g. The microporosity of the sample was measured using an Autosorb-1MP BET analyzer (Quantachrome) equipped with a 1-mm Hg pressure transducer. The density functional theory (DFT) method was used to obtain the pore size distribution, which is presented in Figure 2.2 as the differential specific surface area contained within the pores.

Figure 2.2. The pore size distribution of the quartz sample.

Figure 2.3. Particle size distribution of the quartz sample

The particle size distribution of the quartz sample, as determined with the use of a Malvern Mastersizer 2000, fell entirely in the range from 0.3 to 13.8 microns with a volume-average size of 2.3 microns (Figure 2.3). The specific surface area calculated from the size distribution, assuming perfectly spherical and smooth particles, was 1.5 m²/g.

The cumulative fraction of the specific surface area contained in the pores smaller than 62 Å was 4.3 m²/g. The difference between the total BET area and the internal pore surface area is 1.7 m²/g and agrees reasonably well with the value calculated from the size distribution. Since the radius of gyration of guar gum in aqueous solutions is about 980 Angstroms (Frollini et al., 1995), the polymer cannot enter any of the pores shown in Figure 2.2. Thus the value of 1.7 m²/g was used for calculating the polymer adsorption densities since that is the external surface area accessible to guar gum.

Cesium chloride (crystalline, 99.9% pure), cesium hydroxide (50 wt% aqueous solution, 99% pure) and lithium hydroxide (crystalline, 98%+ pure), were supplied by Aldrich. Lithium, sodium and potassium chlorides, as well as sodium and potassium hydroxides, were all ACS-certified chemicals from Fisher. In some tests, hydrochloric acid (Fisher) was also used for pH adjustments.

All the experiments were carried out in the pH range from 3 to 11, i.e. on the alkaline side of the point of zero charge when the quartz surfaces were negatively charged.

2.2 Methods

2.2.1. Adsorption tests

In the adsorption tests, 5 g of quartz was first conditioned with 12.5 ml of salt solution or distilled water in a thermostated shaker for 20 minutes. Before conditioning, desired pH values were approximately set by adding concentrated solutions of HCl, LiOH, NaOH, KOH or CsOH to the samples. Then 12.5 ml of a guar gum solution of known concentration were added and the entire mixture was conditioned for 1 hour. Afterwards, the samples were centrifuged to remove quartz and the supernatant was assayed for guar gum following the phenol-sulfuric acid method developed by Dubois et al (1956) for polysaccharides. At this point, the pH of the supernatants was measured and reported. Dextrin assays were performed with the same procedure. The calibration curve for dextrin is shown in Appendix 2.

The analytical procedure for the phenol-sulfuric acid method involved the following steps. First, a 4-ml aliquot of a supernatant was transferred to a beaker. Second, 1.5ml of a 60g/dm³ phenol solution was added to the sample. Then, 10 ml of concentrated sulfuric acid was carefully introduced while thoroughly stirring to avoid excessive boiling and hence spilling of the mixture. First 2-3 ml of the acid were added drop by drop, and the remaining amount was allowed to flow freely. The reacting mixture was stirred again and left to cool at room temperature for 30 minutes. Depending on the concentration of guar gum in solution, the reacting mixture acquires a more or less intense yellow color with the maximum absorbance at 488 nm. The absorbance of each sample was measured at 488 nm using a Cary 50 UV-VIS spectrophotometer (Varian). The guar gum concentration was read from a calibration curve (Appendix 1).

In all cases, blank samples were prepared by conditioning 5 g quartz with 25 ml of an appropriate salt solution or distilled water. The amount of guar gum adsorbed was calculated from the difference between the initial (known) and equilibrium (measured) concentrations.

The amount adsorbed was calculated from the following formula:

$$A = \frac{(C_{in} - C_{Eq.}) \times 0.025L}{5g \times S_{BET}}$$

Where A is amount of guar gum adsorbed, C_{in} is the initial guar gum concentration (known), $C_{Eq.}$ is the equilibrium guar gum concentration (measured), and S_{BET} is the specific surface area ($1.7m^2/g$).

The standard deviation in these experiments was 2-5%.

2.2.2. Zeta Potential Measurements

In order to correlate the adsorption of alkali metal cations on quartz with the colloidal stability of the quartz suspensions, a series of zeta potential measurements was carried out. In addition, since ion diffusion at the quartz-solution interface can affect the measured zeta potentials, a number of tests were performed for long and short conditioning times with the background electrolytes.

The zeta potential studies were performed through electroacoustic measurements using a Colloidal Dynamics ZetaProbe. The zeta potential was calculated using O'Brien's model (O'Brien, 1988; O'Brien, 1990; O'Brien et al., 1995). The tests were carried out at 10% (wt) solids. Electrokinetic Sonic Amplitude (ESA) is an electroacoustic effect that occurs when an alternating electric field of known amplitude and frequency is applied to a suspension of fine charged particles. The electric field causes the particles to move back and forth (oscillate) due to their surface charges, and in so doing each particle generates a tiny pressure wave of some amplitude and frequency. The velocity of this oscillatory motion is proportional to the surface charge of the particles. All the pressure waves then add up to a macroscopic sound wave that travels through the suspension to the measuring electrodes coupled with pressure transducers (Hunter, 1993).

As the frequency of the applied field is increased, the inertial forces acting on the particles increase causing both a decrease in the magnitude of particle mobility and an increase in the phase lag between the applied field and measured signal. This simply means that small particles easily keep up with changes in the electric field, while the ESA signal from large particles is significantly delayed with respect to the applied field, particularly at higher field frequencies. At low frequencies, when particles are able to quickly respond to any changes in the electric field, the inertia effects can be neglected (Hunter, 1993).

The pH of the quartz suspensions was adjusted to 11 with the corresponding base to avoid introducing foreign cations, and then the zeta potential measurements were performed as automatic titrations from high to low pH using 2.0 M HCl as the titrant. After pH adjustment the suspension was allowed to equilibrate while stirred for 5 minutes before the zeta potential measurement was performed. The zeta potential of quartz was measured in 0.01 and 0.1 M alkali metal chloride solutions.

The background electrolyte ions can also produce an ESA signal, usually significant at salt concentrations above about 0.01 - 0.1 M concentrations. For this reason the background electrolyte signal was measured and subtracted from the total signal only for 0.1M salts. For each suspension measured, a salt solution of the same salt type and concentration as in the continuous phase of the suspension was prepared. The background signal of these solutions was measured at pH 5.8 and subtracted from the total signal measured for the corresponding suspension at all pH values investigated.

The difference between two titration runs under the same conditions was less than 3 mV.

2.2.3 Turbidity

Turbidity measurements are a simple and convenient tool to study the flocculation process. As the flocculated particles grow in size, their settling rates increase. After a given period of time, the amount of solids left in suspension is a measure of the effectiveness of flocculation. Strongly flocculated suspensions produce very clear supernatants of very low turbidities, while poorly flocculated or dispersed systems remains turbid over a long period of time.

Changes in the turbidities of the quartz-guar gum suspensions were measured with a Hach Model 2100AN Laboratory Turbidimeter. The instrument is a nephelometer, comprised of a 90 deg detector to monitor scattered light, a forward-scatter light detector, a transmitted-light detector, and a back-scatter light detector.

The experiments were performed by first conditioning 0.5g quartz with 50 ml of salt solutions or distilled water in a thermostated shaker for 20 minutes, then adding 50 ml guar gum solution and conditioning for 1 hour. Finally, the samples were allowed to settle for 10 minutes, the supernatants of which (30 ml) were collected as representative samples to measure turbidities. When fully dispersed by high pH in distilled water, the turbidity of a reference quartz suspension was just below the upper measuring limit of the instrument.

The experimental error (standard deviation) in these tests was about 200 NTU at a turbidity of 6500 NTU.

CHAPTER 3 Results

3.1 Zeta Potential Measurements

As Figures 3.1 and 3.2 demonstrate, the magnitude of the zeta potential of quartz particles at any pH value follows the Hofmeister series. The zeta potentials are most negative in the presence of lithium and least negative in the presence of cesium. The results indicate that cesium cations adsorb at the quartz-solution interface in higher quantities than lithium, thus more efficiently screening the negative surface charges around the quartz particles, and hence decreasing the magnitude of the zeta potential.

Figure 3.1. Zeta potential of quartz in 0.01 M solutions of salts.

The zeta potential results show that increasing concentrations of the electrolytes compress the electrical double layer around quartz particles. The absolute values of the zeta potentials are more negative in 0.01 M salt solutions than in 0.1 M salt solutions. In comparison to the trends in 0.01M electrolytes, the same qualitative differences between individual salts can be seen in 0.1M solutions.

Figures 3.3 to 3.6 indicate that no significant effect of prolonged conditioning with the electrolytes, over a period of 24 hours, on the measured zeta potentials was observed.

Figure 3.2 Zeta potential of quartz in 0.1 M solutions of salts.

Figure 3.3 Zeta potential of quartz in 0.01M CsCl, conditioned for 30 minutes and 24 hours.

Figure 3.4 Zeta potential of quartz in 0.01M KCl, conditioned for 30 minutes and 24 hours.

Figure 3.5 Zeta potential of quartz in 0.01M NaCl, conditioned for 30 minutes and 24 hours.

Figure 3.6 Zeta potential of quartz in 0.01M LiCl, conditioned for 30 minutes and 24 hours.

Figure 3.7 The effect of guar gum addition on the zeta potential of the quartz particles. Guar gum concentration 120 mg/L.

Figure 3.7 illustrates the effect of guar gum addition (at 120 mg/L) on the zeta potential of the quartz particles. The guar gum concentration was such that the adsorption density of the polymer was at its plateau so the surfaces of the particles were saturated with the polymer. Even though there is a clear decrease in the magnitude of the zeta potential values, compared to the curves from Figure 3.1, there are still the same relative differences between the results for different background electrolytes.

3.2 Adsorption Measurements

Figures 3.8 and 3.9 present adsorption isotherms of guar gum onto quartz at a pH value of 5.2 (natural pH for the quartz suspensions) in distilled water, in the presence of 0.01M, and 0.1M alkali metal chlorides. In 0.01M electrolytes, the data for guar gum fall on two curves. The adsorption densities of guar gum in distilled water, 0.01M sodium chloride, and 0.01M lithium chloride do not differ significantly, while the amount of guar gum adsorbed on quartz almost doubles in the presence of 0.01M cesium and potassium chlorides. There is a marked increase in the adsorption density for all 0.1M salts (Figure 3.9) compared to the results in 0.01M electrolytes, but still cesium and potassium chlorides give consistently higher adsorption densities than sodium and lithium.

Figure 3.8 Adsorption isotherms of guar gum on quartz at pH 5.2 and alkali metal chloride concentration of 0.01M. A set of adsorption results for a dextrin sample is also included.

In contrast, the adsorption densities of dextrin in distilled water are very low –less than 0.05 mg/m^2 at an equilibrium concentration of 95 mg/L – and the adsorption isotherms are linear. Even though the affinity of dextrin towards quartz is low, Figure 3.8 indicates that there is a small but measurable increase in dextrin adsorption in 0.1 M KCl .

Figure 3.9 Effect of ionic strength on the adsorption of guar gum at pH 5.2.

The apparent effect of pH on guar gum adsorption in distilled water is illustrated in Figure 3.10. It should be pointed out that since the natural pH of the quartz-distilled water system was 5.2, only values higher than 5.2 required hydroxide addition. All pH values below 5.2 were set using hydrochloric acid so no metal cations were introduced into the system below pH 5.2. Seemingly, additions of potassium and cesium hydroxides bring about an increase in the adsorption of guar gum, while sodium and lithium hydroxides have practically no effect.

Figure 3.10 Effect of pH on guar gum adsorption on quartz. pH adjustments were made with various hydroxides or with hydrochloric acid. Initial guar gum concentration 90 mg/L.

As Figure 3.11 shows, this apparent effect of pH in Figure 3.10 is not really due to changes in the pH values, but results from increasing concentrations of metal cations introduced with the strong bases at higher pH. pH 11 is equivalent to a cation concentration of 0.001M. It is noteworthy that once a background electrolyte is present in the system, the “effect” of pH (KOH and CsOH addition) disappears. The adsorption data fall on two curves in a way similar to the data in Figures 3.8 and 3.9. These results confirm the notion that it is the concentration of the monovalent cations that determines the magnitude of guar gum adsorption.

Figure 3.11 Adsorption of guar gum as a function of pH in the presence of 0.01 M background electrolytes. Initial guar gum concentration 90 mg/L.

Some of the most significant results are illustrated in Figure 3.12 which shows the adsorption density as a function of pH when two different cations are present in the guar gum-quartz system – one from the background salt and one from the base. Interestingly, when NaCl is used to provide constant ionic strength, additions of KOH produce the same effect as in Figure 3.10 and guar gum adsorption increases at higher pH values. The same observation can be made for the LiCl-KOH combination - pH adjustments with the use of KOH clearly increase the adsorption density of guar gum. The results for the NaCl-KOH and LiCl-KOH combinations are very similar to the potassium and cesium curves in Figure 3.10. However, when KCl is used as the background electrolyte, NaOH additions do not affect the adsorption of the polymer. It may thus be concluded that it is the presence of potassium ions (and very likely cesium ions) that determines the response of the mixed electrolytes.

Figure 3.12 Co-effect of background electrolyte and added base on the adsorption of guar gum. Initial guar gum concentration 90 mg/L.

Figure 3.13 further demonstrates the co-effect of K^+ and Na^+ on guar gum adsorption. While the total ionic strength was kept constant at 0.01M, adsorption of guar gum increased with increasing amounts of KCl, which confirms that potassium ions determine the response of mixed electrolytes.

The data therefore strongly suggest that Na^+ and Li^+ ions are truly indifferent in dilute solutions while potassium and cesium are capable of enhancing guar gum-quartz interactions even at concentrations as low as 10^{-5} mol/L (pH 9 adjusted with KOH or CsOH). Sodium and lithium cations start affecting guar gum adsorption at concentrations of the order of 0.1M.

Figure 3.13 Co-effect of KCl and NaCl on the adsorption of guar gum at natural pH (5.2). Ionic strength 0.01 M. Initial guar gum concentration 120 mg/L.

3.3 Turbidity Measurements

Effect of alkali metal ions on the stability of quartz particles towards aggregation is demonstrated in Figure 3.14. Turbidity values were expressed in nephelometric turbidity units (NTU). The results indicate that at a given electrolyte concentration turbidities increase according to the sequence $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$, with Li^+ producing the highest turbidities. In other words, aggregation of quartz is stronger in the presence of Cs^+ than in the presence of Li^+ . In addition, turbidities decrease with increasing electrolyte concentrations.

Figure 3.14 Effect of alkali ions on the stability of quartz (pH 5.2).

Figure 3.15 illustrates the effect of guar gum on the colloid stability of the guar gum-quartz suspensions in the presence of 0.01M alkali metal chlorides at pH 5.2. Guar gum acts as a flocculant towards quartz particles. The flocculation of quartz by guar gum in distilled water is rather weak. In the presence of all the salts even traces of the polysaccharide produce supernatants with the clarity of pure water. As the guar gum concentration increases, the results again tend to fall on two curves; one for Li^+ and Na^+ , and one for Cs^+ and K^+ . In 0.01M sodium and lithium chlorides, the turbidity of the system can easily be brought back to that of the quartz-distilled water system, while

much higher concentrations of guar gum are needed to sterically redisperse the quartz particles in the presence of cesium and potassium.

Figure 3.15 Turbidity of the guar-quartz system in the presence of 0.01N electrolytes at natural pH.

Flocculation of quartz by guar gum is still possible even at pH 10 (Figure 3.16). The data again fall on two curves but maximum flocculation (lowest turbidity) in the presence of sodium and lithium is significantly weaker compared to cesium and potassium. At pH 10 increasing guar gum concentrations more readily redisperse the system than at pH 5.2 but full redispersion again appears to be very difficult in the presence of potassium and cesium. The restabilization of the system at pH 10 seem to be aided by stronger electrostatic repulsion between the particles.

As shown in Figure 3.17, the system is destabilized towards aggregation even further in 0.1M electrolytes, and full redispersion of quartz is impossible in the studied guar gum concentration range. The turbidity values for Cs and K are very low and it is difficult to conclude whether the data fall on the same curve, but there are some measurable differences between sodium and lithium cations.

Figure 3.16 Turbidity of the guar gum-quartz system in the presence of 0.01M electrolytes at pH 10.

Figure 3.17 Turbidity of the guar gum-quartz system in the presence of 0.1M electrolytes at natural pH.

CHAPTER 4 Discussion

The affinity of alkali metal cations towards silica surfaces generally follows the Hofmeister series (Li^+ , Na^+ , K^+ , Cs^+) with cesium cations adsorbing in greater quantities than lithium (Tadros and Lyklema, 1968; Sonnefeld et al., 1995). This trend also manifests itself in the zeta potential results for the quartz sample (Figure 3.1 and 3.2) with cesium producing the least negative zeta potentials. Such enhanced adsorption for a series of ions of the same charge but of a different size is typically interpreted in terms of some sort of poorly defined, non-electrostatic “specific interaction” (Tadros and Lyklema, 1968; James and Healy, 1972; Lyklema, 2003) between the surface and the ions.

Tadros and Lyklema (1968) and Lyklema (1968) postulated that the observed differences in the adsorption densities of alkali metal cations at the silica-solution interface were largely determined by the ability of the ions to penetrate a porous, gel-like surface layer present around the silica particles. Thus, less hydrated, effectively smaller cesium and potassium cations exhibit higher affinities towards such a surface compared to larger strongly hydrated lithium and sodium ions.

Vermeulen and Cantwell (1995) reported similar diffusion effects for sodium ions adsorbing on a fused silica-type of surface. The slow diffusion of sodium manifested itself by a drift of the zeta potential towards an “equilibrium” value. Interestingly, Tadros and Lyklema stated that conditioning times between 30 and 90 minutes were necessary to achieve constant electromotive force readings during potentiometric titrations of silica suspensions in the presence of alkali metal chlorides (Tadros and Lyklema, 1968). Long conditioning times were also required in electroosmotic studies of the silica-solution interface (Huang et al., 1993).

Even though the quartz sample used in this study was microporous (Figure 2.2), no significant effect of prolonged conditioning with the electrolytes, over a period of 24 hrs, on the measured zeta potentials was observed suggesting that ion diffusion effects

were not pronounced in the studied system. It should also be pointed out that crystalline minerals are less soluble than amorphous ones so the formation of a "gel layer" is less likely to occur on quartz than on amorphous silica.

It is interesting to note that even though the four cations adsorb in different quantities on quartz, as seen from the zeta potential results, only two sets of data are consistently observed in guar gum adsorption; those in the presence of Cs and K, and those for Li and Na. The same can be said about the flocculation of quartz. As expected, in the absence of guar gum the coagulating power of the background cations towards quartz increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ and this trend correlates well with the decreasing magnitude of the zeta potentials (Figure 3.1). The zeta potentials of guar-coated quartz particles are also different in the presence of the four cations, even under the conditions of surface saturation by the polymer, and yet the stability results do not follow four different curves. Although hydrogen bonding is weaker than electrostatic repulsion, it seems that, regardless of the type of the background electrolyte, hydrogen bonds between the quartz surface and the polysaccharide are sufficiently numerous to overcome electrostatic repulsive forces between the negatively charged quartz particles and to cause bridging flocculation. Therefore, the stability of the quartz-guar gum system correlates much better with the adsorption density of the polymer rather than with the magnitude of electrostatic repulsion. The fact that the adsorption data fall on two curves suggests that there is a threshold "value" of the structure-breaking capabilities of the alkali metal cations for disrupting the interfacial water and enhancing guar gum adsorption. Following the arguments developed by James and Healy (1972), this critical transition should be related to the hydration energy of the cations.

The results also suggest that guar gum adsorption does not interfere with the charging mechanism of the quartz surface and the adsorbed macromolecules simply move the shear plane farther away from the mineral surface thus decreasing the magnitude of the zeta potential.

Flocculants are most efficient at adsorption densities corresponding only to a fraction of the complete surface coverage (Kitchener, 1972). This agrees well with the turbidity results that show that quartz flocculation is most pronounced at very low initial guar gum concentrations. At higher polymer adsorption densities, steric stabilization takes place and brings about redispersion of the quartz particles. As the guar gum concentration increases, the conditions for the onset of steric stabilization, i.e. surface saturation by the polymer, are met first in the presence of sodium and lithium. Significantly higher concentrations of the polysaccharide are necessary to reach the saturation level for cesium and potassium and to induce steric effects. As the initial concentration of guar gum gradually increases, there is a critical guar gum dosage at which the quartz surface becomes saturated by the polymer in the presence of Li and Na, but the adsorption density in the presence of K and Cs at this critical initial dosage is still far from saturation. In other words, at such a transition concentration, steric effects start redispersing the quartz suspensions in the presence of Li and Na, but flocculation will still proceed in the presence of K and Cs until the saturation level is reached at higher guar gum dosages. It is not the absolute adsorption density that determines the onset of steric stabilization, but rather a relative/fractional coverage of the surface. These observations generally explain well the fact that the stability of the guar gum-quartz system at a given guar gum concentration is always better in the presence of sodium and lithium than in the presence of cesium and potassium.

Based on these results, the following mechanism of guar-quartz interactions is suggested. Guar gum adsorption on quartz should be viewed as competing with the adsorption of water molecules since the same adsorption sites are most likely involved in both processes if hydrogen bonding is assumed to be the driving mechanism. When a water-structure-making cation approaches the negatively charged quartz surface its presence does not change the interfacial water structure and therefore does not affect the "competition equilibrium" – the same amount of the polysaccharide adsorbs in water as in a structure maker solution. In this context, it is noteworthy that the hydrogen cation is also a water-structure maker.

In contrast, structure-breaking regions around potassium and cesium ions, combined with higher adsorption of these ions, produce areas of disturbed water layers on the quartz surface thus allowing guar gum to attach itself to the now more accessible surface silanol groups. Both the hydroxyl groups of the polysaccharide and the surface silanol groups on quartz are hydrated in aqueous solutions. For a hydrogen bond to form between the polymer and the surface, the hydration water must somehow be removed. The postulate that a structure breaking cation can cause such an effect and facilitate adsorption seems to be in-line with this type of reasoning.

The proposed interpretation agrees well with the recent observation that structure-breaking ions in concentrated brines can displace interfacial water molecules from a hydrophilic solid surface to such an extent that the surface becomes slightly hydrophobic (Hancer, 2001).

It is noteworthy that none of the studies referenced in the literature review section provide any discussion or explanation as to which polysaccharides are “allowed” to break through the tight layer of water molecules on the mineral surface and form all the different types of direct bonds with the surface. In other words, the presence of the interfacial water and the effect of structure-making or breaking capabilities of background electrolytes (usually sodium or potassium salts) on polysaccharide adsorption have so far been completely ignored.

There are no systematic data available on interactions between guar gum and alkali metal cations in dilute electrolyte solutions. Recent viscosity measurements for a number of modified guar gums indicate that guar gum molecules are not affected by potassium nitrate concentrations up to 0.1M (Shortridge et al., 2000). Some limited results obtained in concentrated electrolytes suggest that guar gum is extremely stable at high ionic strengths (~3M salts) in terms of its solubility and ability to maintain high viscosity (Pawlik and Laskowski, 2004; Maier et al., 1993) indicating that the conformation of the polymer in solution does not change with electrolyte additions. Gittings et al. (2001) found that the fractal dimension of guar gum changed very little in

1M NaCl compared to that in distilled water. Such observations typically mean that polymer-cation interactions are not strong even in concentrated salt solutions. On the other hand, Napper found that aggregation of a sterically stabilized dispersion (polyvinyl acetate stabilized by polyethylene oxide) could be induced in 2-molar alkali metal chloride solutions at higher temperatures (50-90 °C) (Napper, 1970). This type of coagulation is caused by changes in the "goodness" of the solvent resulting from increasing polymer-polymer interactions and diminishing polymer-solvent interactions in the presence of electrolytes. The coagulating power of alkali metal cations in destabilizing such systems was opposite to what one would expect if the simple "salting-out" mechanism was assumed, i.e. lithium cation, the most hydrated ion in the series, was the weakest coagulant (Napper, 1970). Napper attributed the observed behavior of the ions to their water structure-making or breaking capabilities, but also indicated that such a response is probably very system-specific.

In this work, it was assumed that polymer-alkali metal ion interactions were negligible in the overall phenomenon, at least at the electrolyte concentration levels and temperatures studied. In this respect it should also be pointed out that, due to electrostatic attraction between the negatively charged quartz surface and cations in solution, the concentration of the cations at the negatively charged quartz surface is much higher than in the bulk solution. Therefore, the effect of the alkali metal cations on the interfacial water is much more significant than any effects related to the hydration of guar gum.

The "indifferent character" of alkali metal cations should perhaps be revisited. While low concentrations of sodium and lithium affect the quartz-guar gum system only by compressing the electrical double layer around the quartz particles, potassium and cesium additionally disturb the structure of the interfacial water and thus affect the adsorption of the polymer. From this point of view, the apparent effect of pH is noteworthy as it may lead to erroneous conclusions if the effect of the cation is not "decoupled" from the true effect of the surface charge. This type of pH and ionic strength-dependent adsorption is typically associated with adsorption of ionic polymers.

In solutions containing both structure-making and structure-breaking ions, it is the structure breaker that controls the response of the system (Figures 3.12 and 3.13). Such mixed solutions are very common in mineral processing. The usual assumption that the role of the electrolytes is just to provide constant ionic strength may not be sufficient to fully understand the underlying mechanisms. As the data show, a sodium chloride concentration of 0.01M does not produce any effect of ionic strength on guar gum adsorption (with respect to distilled water), while the same concentration of KCl does (Figure 3.8).

In more concentrated electrolyte solutions ($\sim 0.1\text{M}$) additional factors should also be considered, e.g. competitive hydration between the ions and the polymer, solvency effects, and the conformation of guar gum molecules. Clearly, additional work is needed to elucidate the role of such effects in guar gum adsorption.

As reported in many studies, guar gum exhibits high-affinity type of adsorption on various mineral surfaces which is quite inconsistent with the assumed weak hydrogen bonding interactions between the polymer and the mineral surfaces. As demonstrated in this study, very high affinity adsorption isotherms were also obtained for the quartz sample. According to the acid-base interaction model of polysaccharide adsorption proposed by Liu et al. (2000), guar gum should not adsorb on the acidic quartz surface in such high quantities. The relatively high molecular weight of the polysaccharide, and hence increased chemical affinity compared to shorter chain polymers (e.g. dextrin), can account to some extent for such adsorption behavior. The randomness of substitution of the polymannose main chain by galactose is never perfect. The least substituted sections of the guar molecules show the greatest tendency to associate and precipitate, while the more densely substituted regions serve to solubilize the polymer chain (Dea, 1993). It is reasonable to assume that in a natural guar gum solution a fraction of the macromolecules form intermolecular entanglements which could adsorb on the solid surface. This "aggregate" adsorption of entire entanglements would well explain the high adsorption densities. Unfortunately, this type of particulate effects in polysaccharide adsorption have never been adequately studied.

As indicated earlier, the adsorption of dextrin on quartz is very low and in contrast to guar gum the effect of the background electrolyte is not so obvious. Thus the described effect of alkali metal cations on guar gum adsorption is also related to the molecular weight of adsorbing polysaccharides. A similar effect of alkali metal chlorides on the adsorption of a high molecular weight (MW = 5 million) dextran on quartz was also observed (see Appendix 4). The results for dextrin also strongly suggest that the quartz surface was free from metal impurities which would otherwise "activate" the surface resulting in much higher dextrin adsorption densities than the observed ones.

CHAPTER 5 Conclusions

In dilute electrolyte solutions, guar gum adsorption on quartz strongly depends on the water structure-making or breaking properties of the background cations. The adsorption density of the polymer is independent of the pH of the quartz suspensions, but misleading trends may be observed if the effect of the base cation is not separated from the true effect of the surface charge.

Since the adsorption density of guar gum does not change with the surface charge (pH) on the quartz surface, and assuming that the quartz surface is free from impurities, it is postulated that hydrogen bonding is the main adsorption mechanism.

An additional phenomenon in guar gum-quartz interactions is suggested in which water structure-breaking cations disturb the interfacial water layer allowing guar gum to more densely adsorb on the exposed/dehydrated surface silanol groups. Structure-making cations better fit into the interfacial water layer and do not affect the guar gum-water competition for the polar surface sites.

The results strongly suggest that simple alkali metal chlorides are not totally indifferent, and their water-structure making/breaking capabilities should be taken into account to better understand the behavior of a model system such as quartz-guar gum.

Differences in the adsorption densities of guar gum correlate with the stability of quartz suspensions. The flocculation of quartz is much more efficient in solutions of structure breaking ions. At the same time, steric stabilization is much more difficult in the presence of such electrolytes.

RECOMMENDATIONS:

The results of this work show that although NaCl and LiCl did not affect adsorption of guar gum at low concentration (0.01M), they did increase adsorption of guar gum when the salt concentration was high enough (0.1M). However, the mechanism behind this phenomenon is not fully understood. It is possible that there is a transition electrolyte concentration at which solvency effects start to play a dominant role. In concentrated salt solutions, the conformation and hydration of guar gum can be affected significantly, which would influence the adsorption behavior of guar gum. Therefore, additional adsorption studies in concentrated salt solutions need to be carried out to investigate the role of solvency effects in greater detail.

The effect of alkali metal cations also seems to be related to the molecular weight of polymers. For a high molecular weight polymer, i.e. guar gum, its adsorption on quartz increased significantly in the presence of KCl and CsCl, while for a low molecular weight polymer, i.e. dextrin, its adsorption on quartz was not affected by KCl so significantly. Thus it seems that the higher the molecular weight, the more significant the effect of alkali metal cations. Ideally, a series of guar gums of different molecular weights should be used to research this effect. Other polymers adsorbing through hydrogen bonding could also be investigated.

The solids concentration in the reported tests was relatively high. The vast majority of adsorption studies reported in technical literature were performed at much lower solids contents. It is possible that some volume exclusion effects play a role in the adsorption process – guar gum always exhibits a distribution of molecular weights and possibly only certain molecular weight fractions actually adsorb on the mineral surfaces at higher solids contents. Polymer diffusion effects (mixing conditions) are also known to be significant in more concentrated suspensions. A systematic study on the influence of the solids content on the adsorption process is therefore recommended.

REFERENCES

Afenya, P.M., Adsorption of xanthate and starch on synthetic graphite, *International Journal of Mineral Processing*, vol. **9**, pp. 303–319, (1982).

Balaji, S.R. and Iwasaki, I., Adsorption mechanism of starches in flotation and flocculation of iron ores, *Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers*, vol. **244**, pp. 401–406, (1969).

Barfod, N. M., Calcium and water-binding activity during alginate gelation. In Philips, G. O., Williams, P. A., and Wedlock, D. J. (Eds.), *Gums and Stabilizers for the Food Industry*, vol. **4**, IRL Press, Oxford, (1988).

Bergna, H. E., Colloidal chemistry of silica. In Bergna, H.E. (Ed.), *The Colloidal Chemistry of Silica*, American Chemical Society, Washington, D. C., (1994).

Bilgen, E., Expansion/contraction behavior of dilute polymer solutions, *Canadian Journal of Chemical Engineering*, vol. **49**, pp. 732-736, (1972).

Blanshard, J. M. V., Stabilizers-their structure and properties, *Journal of the Science of Food and Agriculture*, vol. **21**, pp. 393-399, (1970).

Bockris, J. O'M. and Khan, S. U. M., *Surface Electrochemistry*, Plenum Press, New York, (1993).

Bockris, J. O'M. and Reddy, A. K. N., *Modern Electrochemistry*, Plenum Press, New York, (1998).

Bohmer, M. R. and Koopal, L. K., Adsorption of ionic surfactants on variable-charge surfaces. 1. Charge effects and structure of the adsorbed layer, *Langmuir*, vol. **8**, pp. 2649-2659, (1992).

Bolt, J. H., Determination of the charge density of silica sols, *Journal of Physical Chemistry*, vol. **61**, pp. 1166-1169, (1957).

Chatterji, J. and Borchardt, J. K., Application of water-soluble polymers in the oil field, *Journal of Petroleum Technology*, vol. **33**, pp. 2042-2056, (1981).

Cheng, Y., Brown, K. M. and Prud'homme, R. K., Characterization and intermolecular interactions of hydroxypropyl guar gum solutions, *Biomacromolecules*, vol. **3**, pp. 456-461, (2002).

Chialvo, A. A., Cummings, P. T., Simonson, J. M. and Mesmer, R. E., Solvation in high-temperature electrolyte solutions. II. Some formal results, *Journal of Chemical Physics*, vol. **110**, pp. 1075-1086, (1999).

Davis, J. A., James, R. O. and Leckie, J. O., Surface ionization and complexation at the oxide/water interface, *Journal of Colloid and Interface Science*, vol. **63**, pp. 480-499, (1978).

Dea, I. C. M., Conformational origins of polysaccharide solution and gel properties. In: Whistler, R. L. and Bemiller, J. N. (Ed.), *Industrial gums — polysaccharides and their derivatives*, Third edition, Academic Press, (1993).

De Xammar Oro, J. R., Role of co-solute in biomolecular stability: glucose, urea and water structure, *Journal of Biological Physics*, vol. **27**, pp. 73-79 (2001).

Drost-Hansen, W., Effects of vicinal water on colloidal stability and sedimentation processes, *Journal of Colloid and Interface Science*, vol. **58**, pp. 251-262, (1977).

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F., Colorimetric method for determination of sugars and related substances, *Analytical Chemistry*, vol. **28**, pp. 350-356, (1956).

Dumont, F., Warlus, J. and Watillon, A., Influence of the point of zero charge of titanium dioxide hydrosols on the ionic adsorption sequences, *Journal of Colloid and Interface Science*, vol. **138**, pp. 543-554, (1990).

Duval, Y., Mielczarski, J. A., Pokrovsky, O. S., Mielczarski, E. and Ehrhardt, J., Evidence of the existence of three types of species at the quartz-aqueous solution interface at pH 0-10: XPS surface group quantification and surface complexation modeling, *Journal of Physical Chemistry B*, vol. **106**, pp. 2937-2945, (2002).

Fleer, G. J. and Scheutjens, J. M. H. M., Modeling polymer adsorption, steric stabilization and flocculation. In Dobias (Ed.), *Coagulation and flocculation*, Surfactant Science Series 47, pp. 209-263, (1993).

Franks, F., *Water: a Comprehensive Treatise*, Plenum Press, New York, (1972).

Frank, H. S. and Wen, W. Y., Ion-solvent interaction - structural aspects of ion-solvent interaction in aqueous solutions: a suggested picture of water structure, *Discussions of the Faraday Society*, vol. **24**, pp. 133-140, (1957).

Frollini, E., Reed, W. F., Milas, M. and Rinaudo, M., Polyelectrolytes from polysaccharides: Selective oxidation of guar gum — a revisited reaction, *Carbohydrate Polymers*, vol. **27**, pp. 129-135, (1995).

Gittings, M. R., Cipelletti, L., Trappe, V., Weitz, D. A., In, M. and Lal, J., The effect of solvent and ions on the structure and rheological properties of guar solutions, *Journal of Physical Chemistry A*, vol. **105**, pp. 9310-9315, (2001).

Goldstein, A. M. and Alter, E. N., Guar gum. In: Whistler, R. L. Ed., *Industrial gums, polysaccharides and their derivatives*, Academic Press, New York, (1959).

Gregory, J., Flocculation by polymers and polyelectrolytes. In Tadros, T. F. (Ed.), Solid liquid dispersions, Academic Press, (1987).

Gurney, R.W., Ionic Processes in Solution, McGraw Hill Press, New York, (1953).

Haigh, R., Rimmer, S. and Fullwood, N.J., Synthesis and properties of amphiphilic networks. 1: the effect of hydration and polymer composition on the adhesion of immunoglobulin-G to poly (laurylmethacrylate-*stat*glycerolmonomethacrylate-*stat*-ethylene glycoldimethacrylate) networks, Biomaterials, vol. **21**, pp. 735-739, (2000).

Hanna, H. S., Adsorption of some starches on particles of spar minerals. In: Bishay, A. (Ed.), Recent Advances in Science and Technology Materials, vol. **1**, Plenum, New York, pp. 365-374, 1973.

Hancer, M., Celik, M. S. and Miller, J. D., The significance of interfacial water structure in soluble salt flotation systems, Journal of Colloid and Interface Science, vol. **235**, pp. 150-161, (2001)

Haung, H. H., Calara, J. V., Bauer, D. L., and Miller, J. D., Adsorption reaction in the depression of coal by organic colloids, Recent Developments in Separation Science, vol. **4**, CRC Press, pp. 115-133, (1978).

Hayes, K. F. and Leckie, J. O., Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces, Journal of Colloid and Interface Science, vol. **115**, pp. 564-572, (1987).

Hayes, K. F., Papelis, C. and Leckie, J. O., Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces, Journal of Colloid and Interface Science, vol. **125**, pp. 717-726, (1988).

Healy, T. W. and Fuerstenau, D. W., The oxide-water interface-interrelation of the zero point of charge and the heat of immersion, *Journal of Colloid Science*, vol. **20**, pp. 376-386, (1965).

Henniker, J. C., The depth of the surface zone of a liquid, *Review of Modern Physics*, vol. **21**, pp. 322-341, (1949).

Hiemstra, T., De Wit, J. C. M. and Van Riemsdijk, W. H., Multisite proton adsorption modeling at the solid/solution interface of (hydr)oxides: A new approach: II. Application to various important (hydr) oxides, *Journal of Colloid and Interface Science*, vol. **133**, pp. 105-117, (1989).

Horne, R. A., Day, A. F., Young, R. P. and Yu, N.T., Interfacial water structure: the electrical conductivity under hydrostatic pressure of particulate solids permeated with aqueous electrolyte solution, *Electrochimica Acta*, vol. **13**, pp. 397-406, (1968).

Huang, T. L., Tsai, P., Wu, C.T. and Lee, C.S., Mechanistic studies of electroosmotic control at the capillary-solution interface, *Analytical Chemistry*, vol. **65**, pp 2887-2893, (1993).

Hunter, R. J., *Introduction to modern colloid science*, Oxford University Press, (1993).

Iler, R. K., *Chemistry of silica: solubility, polymerization, colloid and surface properties, and biochemistry*, Wiley, New York, (1979).

Ishihara, K., Namura, H., Mihama, T., Kurt, K., Iwaski, Y. and Nakabayashi, N., Why do phospholipid polymers reduce protein adsorption? *Journal of Biomedical Materials Research*, vol. **39**, pp. 323-330, (1998).

James, R. O. and Healy, T. W., Adsorption of hydrolyzable metal ions at the oxide—water interface. III. A thermodynamic model of adsorption, *Journal of Colloid and Interface Science*, vol. **40**, pp. 65-81, (1972).

Jenkins, P. and Ralston, J., The adsorption of a polysaccharide at the talc-aqueous solution interface, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. **139**, pp. 27-40, (1998).

Kaminsky, M., The Concentration and Temperature Dependence of The Viscosity of Aqueous Solutions of Strong Electrolytes III, *Zeitschrift für physikalische chemie (Frankfurt)*, vol. **12**, pp. 206-231, (1957).

Khosla, N. K., Bhagat, R.P., Gandhi, K.S. and Biswas, A.K., Calorimetric and other interaction studies on mineral-starch adsorption systems, *Colloids and surfaces*, vol. **8**, pp. 321-336, (1984).

Kisielew, W. F., Surface phenomena on semiconductors and dielectrics, Nauka, Moscow, (1970).

Kitchener, J. A., Principles of Action of Polymeric Flocculants, *British Polymer Journal*, vol. **4**, pp. 217-229, (1972).

Klier, K. and Zettlemoyer, A. C., Water at interfaces: molecular structure and dynamics, *Journal of Colloid and Interface Science*, vol. **58**, pp. 216-229, (1977).

Lamb, R. N. and Furlong, D. N., Controlled wettability of quartz surfaces, *Journal of the Chemical Society. Faraday Transactions 1*, vol. **78**, pp. 61-73, (1982).

Little, L. H., *Infrared Spectra of Adsorbed Species*, Academic Press, New York, (1966).

Liu, Q. and Laskowski, J. S., The role of metal hydroxides at mineral surfaces in dextrin adsorption, I. Studies on modified quartz samples, *International Journal of Mineral Processing*, vol. **26**, pp. 297-316, (1989).

Liu, Q., Zhang, Y. and Laskowski, J. S., The adsorption of polysaccharides onto mineral surfaces: an acid/base interaction, *International Journal of Mineral Processing*, vol. **60**, pp. 229–245, (2000).

Lyklema, J., The structure of the electrical double layer on porous surfaces. *Journal of Electroanalytical Chemistry*, vol. **18**, pp. 341-348, (1968).

Lyklema, J., Lyotropic sequences in colloid stability revisited, *Advances in Interface and Science*, vol. **100-102**, pp. 1-12, (2003).

Maier, H., Anderson, M., Karl, C., Magnuson, K. and Whisler, R. L., Guar, locust bean, tara, and fenugreek gums. In: Whistler, R. L., and Bemiller, J. N. (Eds), *Industrial gums — polysaccharides and their derivatives*, Third edition, Academic Press, Inc. (1993).

Michelle, L. G., Thomas, W. H. and Lee R. W., Hydrophobicity effects in the condensation of water films on quartz, *Journal of Colloid and Interface Science*, vol. **140**, pp. 450-465, (1990).

Miller, J. D., Laskowski, J. S. and Chang, S. S., Dextrin adsorption by oxidized coal, *Colloids and Surfaces*, vol. **8**, pp. 137–151, (1983).

Miller, J. D., Lin, C. L. and Chang, S. S., Coadsorption phenomena in the separation of pyrite from coal by reverse flotation, *Coal Preparation*, vol. **1**, pp. 21–38, (1984).

Napper, D. H., Steric stabilization and the Hofmeister series, *Journal of Colloid and Interface Science*, vol. **33**, pp. 384-392, (1970).

Napper, D. H., Steric stabilization, *Journal of Colloid and Interface Science*, vol. **58**, pp. 390-407, (1977).

O'Brien, R. W., Electro-acoustic effects in a dilute suspension of spherical particles, *Journal of Fluid Mechanics*, vol. **190**, pp. 71-86, (1988).

O'Brien, R. W., The Electro-acoustic equations for a colloidal suspension, *Journal of Fluid Mechanics*, vol. **212**, pp. 81-93, (1990).

O'Brien, R. W., Cannon, D. W. and Rowlands, W. N., Electroacoustic determination of particle size and zeta potential, *Journal of Colloid and Interface Science*, vol. **173**, pp. 406-418, (1995).

Okazaki, Y., Ishizuki, K., Kawauchi, S., Satoh, M. and Komiyama, J., Ion-specific swelling and deswelling behaviors of ampholytic polymer gels, *Macromolecules*, vol. **29**, pp. 8391-8397, (1996).

Painter, T.J., Gonzalez, J.J. and Hemmer, P.C., The distribution of D-galactosyl groups in guaran and locust-bean gum: new evidence from periodate oxidation, *Carbohydrate Research*, vol. **69**, pp. 217-226, (1979).

Pawlik, M., Laskowski, J. S. and Ansari, A., Effect of carboxymethyl cellulose and ionic strength on stability of mineral suspensions in potash ore flotation systems, *Journal of Colloid and Interface Science*, vol. **260**, pp. 251-258, (2003).

Pawlik, M. and Laskowski, J. S., Effect of ionic strength on stabilization of mineral suspensions by carboxymethyl cellulose and guar gum, 2004 Society for Mining Metallurgy and Exploration (SME) Annual Meeting & Exhibit, Feb. 23-25, Denver, Preprint # 04-059.

Richman, D. and Thomas, H. C., Self-diffusion of sodium in a cation exchange resin, *Journal of Physical Chemistry*, vol. **60**, pp. 237-239, (1956).

Rickayzen, G., Theoretical studies of the solid-fluid interface. In Bee, R. D., Richmond, P. and Mingins, J. (Eds.), *Food Colloidal*, Special Publication series 75, Royal Society of Chemistry, London, (1989).

Rath, R. K. and Subramanian, S., Studies on adsorption of guar gum onto biotite mica, *Minerals Engineering*, vol. **10**, pp. 1405-1420, (1997).

Rath, R. K., Subramanian, S. and Laskowski, J. S., Adsorption of guar gum onto talc. In: Laskowski, J. S. and Poling, G.W. (Eds.), *Processing of Hydrophobic Minerals and Fine Coal*, Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada, pp. 105-119, (1995).

Rath, R. K., Subramanian, S. and Laskowski, J. S., Adsorption of dextrin and guar gum onto talc- a comparative study, *Langmuir*, vol. **13**, pp. 6260-6266, (1997).

Robinson, R. A., *Electrolyte Solutions*, New York Academic Press, (1959).

Robinson, G., Ross-Murphy, S. B. and Morris, E. R., Viscosity-molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan, *Carbohydrate Research*, vol. **107**, pp. 17-32, (1982).

Schufle, S. and Venugopalan, M., Specific volume of liquid water to -40°C , *Journal of Geophysical Research*, vol. **72**, pp. 3271-3275, (1967).

Selected Powder Diffraction Data for Minerals, First Edition, Joint Committee on Powder Diffraction Standards, Swarthmore (PA), Publication DBM-1-23, p. 49, (1974)

Shannon, R. D. and Prewitt, C. T., Effective ionic radii in oxides and fluorides, *Acta Crystallographica - Section B: Structural Crystallography & Crystal Chemistry*, vol. **B25**, pp. 925-946, (1969).

Shortridge, P. G., Harris, Bradshaw, D. J. and Koopal, L. K., The effect of chemical composition and molecular weight of polysaccharide depressants on the flotation of talc, *International Journal of Mineral Processing*, vol. **59**, pp. 215-224, (2000).

Somasundaran, P., Adsorption of starch and oleate and interaction between them on calcite in aqueous solutions. *Journal of Colloid and Interface Science*. vol. **31**, pp. 557–565, (1969).

Sonnefeld, J., Göbel, A., and Vogelsberger, W., Surface Charge Density on Spherical Silica Particles in Aqueous Alkali Chloride Solutions, *Colloid & Polymer Science*, vol. **273**, pp. 926-931, (1995).

Spiegler, K. S., and Coryell, C. D., Electromigration in a cation exchange resin. III. correlation of self-diffusion coefficients of ions in a cation-exchange membrane to its electrical conductance, *Journal of Physical Chemistry*, vol. **57**, pp. 687-690, (1953).

Steenberg, E. and Harris, P. J., Adsorption of carboxymethyl cellulose, guar gum and starch onto talc, sulphides, oxides and salt-type minerals, *South African Journal of Chemistry*, vol. **37**, pp. 85–90, (1984).

Staszczuk, P., Investigations of the properties of water films on quartz surfaces, *Powder Technology*, vol. **41**, pp. 33-40, (1985).

Stokes, R. H., and Mills, R., Viscosity of electrolytes and related properties, Pergamon Press, New York, (1965).

Subramanian, S. and Laskowski, J. S., Adsorption of dextrin onto graphite, *Langmuir*, vol. **9**, pp. 1330-1333, (1993).

Sverieny, D. A., Interpretation and prediction of triple-layer model capacitances and the structure of the oxide–electrolyte–water interface, *Geochimica et Cosmochimica Acta*, vol. **65**, pp. 3643–3655, (2001).

Tadros, T. F., and Lyklema, J., Adsorption of potential-determining ions at the silica-aqueous electrolyte interface and the role of some cations, *Journal of Electroanalytical Chemistry*, vol. **17**, pp. 267-275, (1968).

Takano, M., Ogata, K., Kawauchi, S., Satoh, M. and Komiyama, J., Ion-specific swelling behavior of poly(N-vinyl-2-pyrrolidone) gel: correlations with water hydrogen bond and non-freezable water, *Polymer Gels and Networks*, vol. **6**, pp. 217-232, (1998).

Trompette, J. L., Zajac, J., Keh, E. and Partyka, S., Scanning of the cationic surfactant adsorption on a hydrophilic silica surface at low surface coverages, *Langmuir*, vol. **10**, pp. 812-818, (1994).

Vermeulen, D. M. and Cantwell, F. F., Slow change in the electrical potential at glass and silica surfaces due to Na^+ sorption in the hydrated layer, *Journal of Chromatography A*, vol. **693**, pp. 205-216, (1995).

Wang, J., Somasundaran, P. and Nagaraj, D. R., Adsorption mechanism of guar gum at solid-liquid interfaces, *Minerals Engineering*, vol. **18**, pp. 77-81, (2005).

Weast, R. C., *Handbook of Chemistry and Physics*, 51th edition, CRC Press, Ohio, (1971).

Whistler, R. L., *Industrial gums — polysaccharides and their derivatives*, Second edition, Academic Press, New York, (1973).

Whistler, R. L., and Hymowitz, T., *Guar: agronomy, production, industrial use, and nutrition*, Purdue University Press, West Lafayette, Indiana, (1979).

Wie, J. M., and Fuerstenau, D. W., The effect of dextrin on surface properties and the flotation of molybdenite, *International Journal of Mineral Processing*, vol. **1**, pp. 17-32, (1974).

Yakubu, P. I., Baianu, I. C., and Orr, P. H., Unique hydration behavior of potato starch as determined by deuterium nuclear magnetic resonance, *Journal of Food Science*, vol. **55**, pp. 458-461, (1990).

Yalamanchili, M. R., Atia, A. A., Drelich, J. and Miller, J. D., Characterization of interfacial water at hydrophilic and hydrophobic surfaces by in-situ FTIR/internal

reflection spectroscopy, Processing of Hydrophobic Minerals and Fine Coal, Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada, pp. 3-16, (1995).

Yates, D. E., Levine, S. and Healy, T. W., Site-binding model of the electrical double layer at the oxide/water interface, Journal of the Chemical Society. Faraday transactions 1, vol. **70**, pp. 1807-1818, (1974).

Zhuravlev, L. T., The surface chemistry of amorphous silica, Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. **173**, pp. 1-38, (2000).

APPENDICES

Appendix 1. Calibration Curve for Guar Gum

Appendix 2. Calibration Curve for Dextrin

Appendix 3. Calibration Curve for Dextran.

Appendix 4. Adsorption Isotherms for Dextran on Quartz.

Appendix 5. Data of Adsorption Measurements

Table 1

Numerical data for Figure 3.8 titled "Adsorption isotherms of guar gum on quartz at pH 5.2 and alkali metal chloride concentration of 0.01M. A set of adsorption results for a dextrin sample is also included". Adsorption data for dextrin are in Table 1a.

0.01M KCl			0.01M CsCl		
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
91.1	0.0	0.2681	91.1	0.0	0.2681
109.1	5.8	0.3039	109.1	3.7	0.3100
128.3	18.0	0.3246	128.4	17.1	0.3274
152.4	35.1	0.3449	149.3	31.9	0.3452
162.5	41.9	0.3545	163.0	44.8	0.3475
179.9	52.9	0.3735	179.4	59.2	0.3536
200.0	71.6	0.3776	193.7	69.7	0.3647
0.01M LiCl			Distilled Water		
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
38.4	0.0	0.1129	40.9	0.0	0.1202
57.8	5.0	0.1554	54.2	2.2	0.1527
75.3	18.1	0.1682	74.2	16.0	0.1711
93.4	34.6	0.1728	89.4	27.1	0.1833
111.5	49.6	0.1821	118.3	52.5	0.1935
130.8	66.9	0.1878	132.1	63.8	0.2007
146.5	81.3	0.1918	144.6	75.5	0.2029
0.01M NaCl					
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)			
53.7	0.5	0.1565			
74.0	13.6	0.1776			
91.4	29.0	0.1835			
114.3	45.2	0.2034			
129.6	58.2	0.2101			

Table 1a

Adsorption data for dextrin.

Distilled Water			0.01M KCl		
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
4.6	4.6	0.0000	5.1	3.8	0.0036
11.7	7.2	0.0131	10.3	8.0	0.0068
20.6	15.2	0.0157	21.4	16.1	0.0158
43.2	34.4	0.0259	41.1	32.6	0.0251
62.3	53.3	0.0266	64.1	54.7	0.0276
82.7	73.1	0.0284	81.3	71.2	0.0298
109.9	95.9	0.0412	105.5	91.2	0.0419
125.8	111.5	0.0421	121.4	107.5	0.0410
0.1M NaCl			0.1M KCl		
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
21.4	16.2	0.0154	21.4	13.3	0.0239
61.5	56.8	0.0140	61.5	49.7	0.0349
81.7	75.3	0.0188	81.7	67.1	0.0428
105.5	89.0	0.0484	105.5	85.5	0.0587
0.01M NaCl					
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)			
7.5	7.5	0.0000			
22.1	16.5	0.0166			
61.0	52.1	0.0262			
103.2	89.6	0.0401			
122.0	107.4	0.0430			

Table 2

Numerical data for Figure 3.9 titled "Effect of ionic strength on the adsorption of guar gum at pH 5.2".

0.1 M CsCl			0.1 M LiCl		
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
92.1	0.0	0.2708	58.7	20.0	0.1139
111.8	1.2	0.3250	79.0	24.0	0.1616
131.2	11.8	0.3510	87.6	25.9	0.1813
148.6	23.7	0.3674	94.6	27.1	0.1985
165.2	36.1	0.3798	99.0	28.1	0.2086
182.7	46.9	0.3994	103.3	29.5	0.2170
203.5	67.2	0.4009	106.7	29.6	0.2268
0.1 M KCl			0.1 M NaCl		
Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
90.5	0.0	0.2663	48.6	0.0	0.1430
109.6	0.1	0.3221	67.1	0.9	0.1947
126.7	1.8	0.3673	85.3	11.1	0.2182
144.7	9.8	0.3967	109.6	27.1	0.2426
161.5	20.7	0.4139	126.6	41.7	0.2498
181.7	35.2	0.4308	144.7	55.8	0.2614
202.2	52.8	0.4395			
217.2	65.7	0.4457			

Table 3

Numerical data for Figure 3.10 titled "Effect of pH on guar gum adsorption on quartz. pH adjustments were made with various hydroxides or with hydrochloric acid. Initial guar gum concentration 90 mg/L".

KOH				NaOH			
pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
5.7	90.1	26.8	0.1863	5.5	90.1	27.5	0.1842
6.4	90.1	23.1	0.1972	7.0	90.1	26.5	0.1872
7.3	90.1	19.8	0.2069	7.7	90.1	25.8	0.1890
8.1	90.1	16.8	0.2157	8.5	90.1	25.4	0.1902
8.7	90.1	6.8	0.2451	9.3	90.1	26.7	0.1866
9.5	90.1	0.9	0.2622	10.2	90.1	22.5	0.1988
10.6	90.1	0.0	0.2650	10.5	90.1	22.6	0.1985
LiOH				CsOH			
pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
6.4	90.1	25.5	0.1900	6.6	90.1	21.2	0.2027
6.8	90.1	25.1	0.1911	7.7	90.1	16.4	0.2169
7.7	90.1	26.3	0.1876	8.2	90.1	11.9	0.2301
8.3	90.1	26.9	0.1860	8.4	90.1	6.6	0.2457
9.4	90.1	27.3	0.1846	9.3	90.1	0.0	0.2680
10.5	90.1	26.6	0.1867	10.8	90.1	0.0	0.2756
HCl							
pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)				
3.3	90.1	32.9	0.1683				
4.2	90.1	30.3	0.1758				
4.9	90.1	28.4	0.1814				
5.0	90.1	28.8	0.1803				

Table 4

Numerical data for Figure 3.11 titled "Adsorption of guar gum as a function of pH in the presence of 0.01 M background electrolytes. Initial guar gum concentration 90 mg/L".

0.01M KCl+KOH or HCl				0.01M CsCl+CsOH or HCl			
pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
3.79	90.1	4.4	0.2520	3.32	90.1	1.1	0.2618
5.45	90.1	0.9	0.2622	4.46	90.1	0.0	0.2688
6.16	90.1	1.1	0.2619	5.19	90.1	0.0	0.2686
7.1	90.1	0.6	0.2633	6.5	90.1	0.0	0.2683
7.62	90.1	0.6	0.2633	7.32	90.1	0.0	0.2686
8.44	90.1	0.6	0.2633	8.01	90.1	0.0	0.2684
9.45	90.1	0.6	0.2633	9.2	90.1	0.0	0.2681
10.27	90.1	0.6	0.2633	10.91	90.1	0.0	0.2685
0.01M NaCl+NaOH or HCl				0.01M LiCl+LiOH or HCl			
pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
3.63	90.1	33.2	0.1674	3.43	90.1	33.5	0.1664
5.55	90.1	28.7	0.1806	4.69	90.1	31.1	0.1736
6.69	90.1	26.5	0.1869	5.63	90.1	27.2	0.1850
7.2	90.1	26.6	0.1866	6.42	90.1	29.2	0.1792
8.09	90.1	32.9	0.1682	7.24	90.1	31.7	0.1716
8.11	90.1	33.1	0.1676	8.19	90.1	33.9	0.1653
8.96	90.1	33.0	0.1678	9.32	90.1	36.4	0.1579
9.71	90.1	33.3	0.1672	10.19	90.1	34.8	0.1625
10.35	90.1	28.3	0.1816	10.71	90.1	33.8	0.1655

Table 5

Numerical data for Figure 3.12 titled "Co-effect of background electrolyte and added base on the adsorption of guar gum. Initial guar gum concentration 90 mg/L".

0.01M NaCl+KOH				0.01M LiCl+KOH			
pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)	pH	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)
5.4	90.0	30.4	0.1753	5.4	90.0	33.4	0.1668
6.5	90.0	27.4	0.1842	6.7	90.0	30.7	0.1747
6.9	90.0	26.5	0.1866	7.3	90.0	30.2	0.1761
7.3	90.0	25.6	0.1893	8.3	90.0	30.2	0.1761
8.6	90.0	19.0	0.2088	9.1	90.0	21.8	0.2009
9.5	90.0	10.1	0.2351	9.5	90.0	17.2	0.2145
10.5	90.0	1.8	0.2593	10.5	90.0	1.5	0.2607
0.01M KCl+NaOH							
Ph	Initial Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorbed Amount (mg/m ²)				
6.9	90.0	1.4	0.2608				
7.7	90.0	1.4	0.2608				
8.9	90.0	1.4	0.2608				
9.7	90.0	1.4	0.2608				
10.5	90.0	1.4	0.2609				
10.8	90.0	1.4	0.2608				

Table 6

Numerical data for Figure 3.13 titled “Co-effect of KCl and NaCl on the adsorption of guar gum at natural pH (5.2). Ionic strength 0.01M. Initial guar gum concentration 120 mg/L”.

Fraction of KCl in mixture with NaCl	Equilibrium Concentration (mg/L)	Amount Adsorbed (mg/m ²)
0.0	50.9	0.2036
0.3	23.0	0.2855
0.5	15.1	0.3089
0.8	7.5	0.3311
1.0	0.0	0.3752