OR-0591-6

DOE/PC/80517-T12
(DE89004644)

FOSSIL

Improving the stability of coal slurries: Final report

Fogler, H.S.

Dec 1988

Michigan Univ., Ann Arbor (USA). Dept. of Chemical Engineering

Reproduced and Distributed by:

U.S. DEPARTMENT OF ENERGY
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

DOE PC 80517-
T12

DE89 004644

IMPROVING THE STABILITY OF COAL SLURRIES: FINAL REPORT. Fogler, H.S. (Michigan Univ., Ann Arbor (USA). Dept. of Chemical Engineering). Dec 1988. 99p.

UNCL

Unlimited

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

Price: Printed Copy A06
Microfiche A01

IMPROVING THE STABILITY OF COAL SLURRIES

Final Report

**By
H. Scott Fogler**

December 1988

**The University of Michigan
Department of Chemical Engineering
Ann Arbor, Michigan 48109**

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

CHAPTER

1.	INTRODUCTION	1
2.	PRELIMINARY EXPERIMENTS WITH COAL SLURRIES	6
2.1	Introduction	6
2.2	Experimental	6
2.2.1	Materials	6
2.2.2	Procedures	8
2.3	Results and Discussion	8
3.	MODEL STUDIES WITH LATICES	10
3.1	Experimental	10
3.1.1	Materials	10
3.1.2	Measurements of Flocculation Rate Constant	11
3.1.3	Binding Studies	13
3.1.4	Electrophoresis Measurements	13
3.1.5	pK Measurements	13
3.1.6	Measurements of Steric Layer Thickness by Photon	

	Correlation Spectroscopy	13
3.1.7	Measurements of Radius of Gyration by Static Light Scattering	14
3.1.8	Fourier Transform Infrared Spectroscopy	14
3.1.9	Measurements of Molecular Weight Distribution	14
3.2	Identification of Effective Stabilizers	15
3.2.1	Introduction	15
3.2.2	Results and Discussion	15
3.2.3	Conclusions	18
3.3	Effect of Pretreatment on Stability	19
3.3.1	Introduction	19
3.3.2	Results and Discussion	19
3.3.3	Conclusions	30
3.4	Effect of pH on Stability	31
3.4.1	Introduction	31
3.4.2	Results and Discussion	31
3.4.3	Conclusions	50
3.5	Effect of Nature of Electrostatic Interactions on Stability	51
3.5.1	Introduction	51
3.5.2	Results and Discussion	51
3.5.3	Conclusions	72
3.6	Direct Force Measurements Between Polysaccharide-bearing Surfaces	73
3.6.1	Introduction	73
3.6.2	Experimental	74
3.6.3	Results and Discussion	76
3.6.4	Conclusions	93
4.	PEPTIZATION OF COAL-WATER SLURRIES	94

4.1	Introduction	94
4.2	Experimental	94
4.3	Results and Discussion	94
5.	SUMMARY	96

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

ABSTRACT

Polysaccharides were found to stabilize colloidal dispersions (such as coal particles and polystyrene latex particles) even at high ionic strengths. The stability studies with various kinds of polysaccharides showed that rod-like molecules (such as poly (galacturonic acid) and gum tragacanth) are much more effective stabilizers than highly-branched molecules such as arabinogalactan. This effective stabilization with the rod-like molecules was found to result from the adsorption of polysaccharides on the particles, i. e., the steric stabilization mechanism. The stability induced by these rod-like molecules depends significantly on the solution pH (the degree of dissociation of carboxyl groups in the polysaccharides), the molecular weight and the surface charge of particles. To elucidate this dependence of stability on these parameters, the adsorption isotherms, the zeta potential and the conformation of adsorbed molecules (the steric layer thicknesses) were measured as a function of the solution pH, the molecular weight and the surface charge. Photon correlation spectroscopy studies showed that the conformation of adsorbed molecules is strongly dependent on the solution pH, the molecular weight and the surface charge, suggesting that the dependence of stability on these parameters is due to the change of the conformation of the molecules adsorbed on the surface. In addition, the solution pH has a significant effect on the flocculation behavior of particles and can be modulated to bring about peptization of particles. This type of stabilization is referred to as electrosteric stabilization whereby steric stabilization is induced by changing the electrical properties of the system (the solution pH in this case). The data obtained from these experiments led to the following conclusions.

- 1) The stability increases with the decrease of the solution pH. Here, the steric layer thickness increases as the solution pH decreases owing to the formation of loops and tails.

- 2) The flocculated particles can be peptized by lowering the solution pH owing to the expansion of the steric layer thickness of the adsorbed molecules.
- 3) The conformational change causing the peptization occurs more easily for the negatively charged particles than for the positively charged particles owing to the electrostatic interactions between the particles and the negatively charged polysaccharides.
- 4) The high molecular weight polysaccharides give greater stability than the low molecular weight polysaccharides for a given amount of adsorption because of the greater steric layer thickness.

CHAPTER 1

INTRODUCTION

Recently, there has been a significant interest in the use of hydrocolloids to stabilize colloidal dispersions ranging from food stuffs to coal-water slurries (1). Some hydrocolloids have the advantage that they can stabilize the colloidal system even at relatively low concentrations in the order of 10 ppm. Recently, it has been shown that a complex formulation containing xanthan gum (an acidic polysaccharide) as a key component, was sufficient to prevent cake formation of a 60 wt % coal-water slurry (2). While there was no indication of how the coal particle interacts, an explanation of the mechanism may be suggested from our previous work on the stabilization of polystyrene latices by acidic and nonionic polysaccharides such as gum tragacanth, pectic acid, arabinogalactan and dextran (3).

Gum tragacanth, GT, was found to be quite an effective stabilizer at concentrations in a low ppm range, and this was suggestive of a possible steric stabilization mechanism. Gum tragacanth, GT, is a dried gummy exudation of *Astragalus* (family of Leguminosae) and an acidic polysaccharide containing D-galacturonic acid (4). As a natural product, it is polydisperse, and has been used as a dispersing agent, emulsifier, and a coagulant in food industry (5).

Previous workers have used natural polymers and polyelectrolytes such as lignin sulphonates for similar studies (6) and since sulphonates are strong acids, the ionic strength of the medium was the sole property that could be adjusted to change the amount of charge of these polyelectrolytes as a mean to control stability. Gum tragacanth, GT, on the other hand, has weakly dissociating surface acidic groups, and the solution pH was thought of as an ideal way to vary the amount of charge of GT and to monitor the effect of

such variations on the stability of polystyrene latices. Therefore, as a result of these preliminary findings, a detailed study of the factors bringing about the stability was undertaken.

As the first step in the systematic investigation of the stabilization mechanism of GT, the stability study with each polysaccharides constituting GT has been undertaken since GT is a mixture of polysaccharides.

GT contains two polysaccharide components, tragacanthic acid and arabinogalactan. The tragacanthic acid is based on poly (galacturonic acid) which is a linear chain of 1, 4 linked α -D-galacturonic acid. Three types of side-chains are known, namely, single β -D-xylopyranose, and disaccharide units of 2-O- α -L-fucopyranosyl-D-xylopyranose and 2-O- β -D-galactopyranosyl-D-xylopyranose (7). Arabinogalactan is highly branched, and is based on a core of D-galactose residues to which highly ramified chains of L-arabinofuranose residues are attached (8). The chemical structures are shown in Figs. 1.1, 1.2. Over half of carboxyl groups of tragacanthic acid are known to be esterified (9). As the second step, the effect of filtration on the stability has been examined since we found that the stabilization effect significantly depends on the pretreatment, i. e., the pore size of filter membrane which determines the size of the GT molecules. Therefore, in order to investigate the effects of the pretreatment on the factors of the steric stabilization mechanism such as the steric layer thickness, the zeta potential and the amount of adsorbed polymers, a series of experiments were carried out using the photon correlation spectroscopy, the zeta potentiometer, etc. In addition, in order to obtain the chemical structure and the molecular weight distribution of the GT samples, the FT-IR and the gel permeation chromatographic technique were used.

As the third step, the effect of pH on stability was studied. The amount of GT adsorbed, the electrostatic repulsive force and the conformation were measured as a function of pH. Photon correlation spectroscopy (PCS) was used to measure the steric layer thickness.

Fig. 1.1 Chemical Structure of Tragacanthic acid and Poly (galacturonic acid)

Fig. 1.2 Chemical Structure of Arabinogalactan

As the final step, in order to investigate how the conformational change of PGUA on the surface is influenced by the adsorption affinity between the surface and PGUA, the positively charged amidine polystyrene latex particles were used as well as the negatively charged sulfate polystyrene latex particles. Since PGUA is negatively charged owing to the deprotonation of the carboxyl groups ($pK_a = 2.9$), the adsorption affinity could be enhanced owing to the electrostatic attractive force when the particles are positively charged. The flocculation rate and the amount of adsorption were measured at various pHs. The results with the amidine latex particles were compared with the results with the sulfate latex particles.

CHAPTER 2

PRELIMINARY EXPERIMENTS WITH COAL SLURRIES

2.1 INTRODUCTION

It has been recognized that coal-water slurries can be used as fuel substitutes. One of the advantages with coal-slurries is that they can be transported through pipes over long distances. However, coal particles tend to flocculate and settle, which causes plugging and difficulties of handling. In order to prevent these problems, the interparticle interactions must be controlled. It is known that surfactants or polymers can modulate these interparticle interactions owing to the steric stabilization mechanism. The steric stabilization results from the adsorption of surfactants or polymers on particles.

We have chosen naturally occurring polysaccharides as candidates for the stabilization of coal-water slurries because (1) they can be dissolved in an aqueous medium very easily, and (2) they are relatively inexpensive. Using an acidic polysaccharide, gum tragacanth, GT as a stabilizer, we examined the stabilization effect on coal-water slurries.

2.2 EXPERIMENTAL

2.2.1 Materials

The coal used in these studies was a blend of Eastern Kentucky and West Virginia coals supplied by Detroit Edison. Table 1.1 shows the analysis of this blend. The coal samples were ground into fine particles (mean diameter: 4.48 μm), and used for sedimentation tests. Gum tragacanth was purchased from Sigma Chemical Company, and used as received.

Table 2.1 The Proximate, Ultimate and Spectrographic Analysis of the ash of the coal

---

PROXIMATE ANALYSIS		
	<u>As-received</u>	<u>Dry</u>
% Moisture	7.33	N/A
% Ash	7.73	8.35
% Volatiles	30.33	N/A
% Fixed Carbon	54.61	N/A
% Sulfur	0.78	0.84
B.T.U.	12931	13955

ULTIMATE ANALYSIS	
% Carbon	78.00
% Hydrogen	5.17
% Nitrogen	1.58
% Oxygen	6.06
% Sulfur	0.84
% Ash	<u>8.35</u>
	100.00

SPECTROGRAPHIC ANALYSIS	
% Fe ₂ O ₃	4.90
% Al ₂ O ₃	27.00
% CaO	0.80
% MgO	0.70
% TiO ₂	1.60
% Na ₂ O	0.20
% K ₂ O	2.60
% SiO ₂	<u>62.20</u>
	100.00

2.2.2 Procedures

The sedimentation tests were conducted at room temperature in 250 ml graduated cylinders. The procedure used in the sedimentation tests was as follows.

- 1) A sample of coal slurry is collected for mixing. GT is then added. The mixture of the slurry and GT was mixed in a laboratory blender for 2 minutes.
- 2) The mixture is then allowed to sit for 1 hour.
- 3) This mixture is placed in a cylinder containing an appropriate amount of $MgCl_2$. The cylinder is then inverted ten times to insure mixing.
- 4) Settling is observed for 4 hours. The settling rate is determined by recording the phase boundary.

2.3 Results and Discussion

The sedimentation tests were conducted for the coal slurries with and without GT. The results are shown in Fig. 2.1. The stabilization of coal-water slurries was accomplished effectively with GT. When compared to the current practice of 1-2 % added stabilizing agents, the estimated cost savings are evident. In order to obtain basic understandings of this stabilization mechanism, model systems were used in the following studies.

Fig. 2.1 Effect of GT on Settling of Coal Particles

CHAPTER 3

MODEL STUDIES WITH LATICES

3.1 EXPERIMENTAL

3.1.1 Materials

The GT, polygalacturonic acid, and arabinogalactan used in this study were supplied by Sigma Chemical Company. After polygalacturonic acid and GT were dissolved in 0.085M of sodium chloride solution, the solutions were filtered through membrane filters (0.22 μ m pores). For the study on the effect of pretreatment, the sample which was filtered through 1.20 μ m pores is designated as GT-L whereas the sample which was filtered through 0.22 μ m pores is designated as GT-S. Unless GT is designated as above, GT-S was used. Since the arabinogalactan is completely soluble in a 0.085M-sodium chloride solution, the filtration was not performed.

The polystyrene latex spheres were prepared by a surfactant free procedure. The properties of latex spheres are listed in Table 3.1.

The hydrophobic latex, PSL-2 (sulfate latex, Dia. = 0.30 μ m), and the hydrophilic latex, PSL-3 (carboxyl latex, Dia. = 0.30 μ m), having the same diameter, were used to examine the hydrophobicity of adsorption of GT. On the other hand, the positively charged amidine latex, AL and the negatively charged latex, SL having the same diameter, 0.49 μ m were used to vary the nature of electrostatic interactions between the particles and the polysaccharides. Unless the latex is designated as above, PSL-1 (sulfate latex, Dia. = 0.33 μ m) was used. PSL-2 (sulfate latex, Dia. = 0.30 μ m), PSL-3 (carboxyl latex, Dia. = 0.30 μ m), SL (sulfate latex, Dia. = 0.49 μ m), and AL (amidine latex, Dia. = 0.49

Table 3.1 Properties of Polystyrene Latices

Polystyrene latex	Surface group	pK	Diameter [μm]	Coefficient of variation in diameter [%]	Charge density [$\mu\text{C}/\text{cm}^2$]
PSL-1]	sulfate	< 2	0.33	11.1	-0.77
PSL-2	sulfate	< 2	0.30	2.5	-1.25
PSL-3	carboxyl	~5	0.30	1.9	-7.14
SL	sulfate	<2	0.49	1.0	-4.03
AL	amidine	11.2	0.49	6.9	+12.2

μm) were supplied by Interfacial Dynamics Corporation. The surface functional groups of latex are shown in Fig. 3.1.

3.1.2 Measurements of Flocculation Rate Constant

The flocculation rate was measured by a turbidimetric technique (10). Polystyrene latex spheres were incubated for 2 hours in the GT solution with the ionic strength of 0.085M at 293K. After the incubation, the ionic strength was increased from 0.085M to 0.33M by the addition of magnesium chloride or sodium chloride solution to induce flocculation. The turbidity was measured as a function of time with a DMS Spectrophotometer Model 200 (Varian Inc.). This incubation time (2 hours) was found to be sufficient since the dimensionless stability factor, W , given as Eq. [1] remained the same after an incubation time of 30 minutes or longer.

$$W = k \text{ without polysaccharides} / k \text{ with polysaccharides} \quad [1]$$

$k \text{ without polysaccharides}$: the flocculation rate constant in the
absence of polysaccharides

k with polysaccharides

: the flocculation rate constant in the
presence of polysaccharides

Fig. 3.1 Surface Functional Groups on Latices

The flocculation rate constant was obtained from the slope of the initial 2 minutes of the time-turbidity curve, and the dimensionless stability factor, W , was then calculated from Eq. [1]. The complete details have been described elsewhere (10).

The pH was adjusted with HCl and NaOH. The ionic strength was kept constant for different pH solutions by adding appropriate amounts of sodium chloride.

3.1.3 Binding Studies

Adsorption isotherms for the binding of GT to polystyrene latex spheres were obtained for different pH solutions. This was achieved by first mixing GT and latex spheres for 2 hours at 293K followed by centrifugation at 11500 rpm for 30 min. The ionic strength was adjusted by adding sodium chloride. The concentration of GT in the solution was measured by Phenol-sulfuric acid method (11).

3.1.4 Electrophoresis Measurements

The electrophoretic mobility was determined at 293K with Lazer-Zee Model 500 (Pen Kem Inc.). Since the value for ka is 330 (k : reciprocal of double layer thickness, a : particle diameter), the zeta potential was calculated using the Smoluchowski equation,

$$u = e z / 4 \pi h \quad [2]$$

where u is the mobility, e the dielectric constant, z the zeta potential and h the viscosity of the medium.

3.1.5 pK Measurements

GT was converted into its H-form by cation exchanger (Amberlite IRA-118H, Sigma Chemical Company) and its pK was measured by potentiometric titration at a constant ionic strength of 0.33M.

3.1.6 Measurements of Steric Layer Thickness by Photon Correlation Spectroscopy (PCS)

PCS data were obtained using Lexel 2 watt Argon ion laser with ITT FW-130 Photo Multiplier Tube. Various angles (50° - 100°) and volume fractions of latex particles ($0 - 1.9 \times 10^{-6}$) were used to confirm that there is no effect of dust or particle-particle interactions. The steric layer thickness was then calculated as the difference in the radii of bare and covered particles obtained from the diffusion coefficient using the Stokes-Einstein relation.

3.1.7 Measurements of Radius of Gyration by Static Light Scattering

The radius of gyration, R_g , was measured using the same laser apparatus used for the measurement of the steric layer thickness. The intensities of the light scattered were obtained at several different angles (30° - 70°), and R_g was calculated from the Zimm Plot.

3.1.8 Fourier Transform Infrared Spectroscopy

A ten mg (dry weight) of GT was mixed with 150 mg of dried KBr, and the mixture was ground, then, was dried in the vacuum-oven for 2 hours. After the sample was pelletized, the FT-IR spectra were obtained using Nicolet 60-SX.

3.1.9 Measurements of Molecular Weight Distribution

The molecular weight distribution was determined by gel permeation chromatography, GPC. Sepharose 4B/CL-4B (Pharmacia Inc.) was used for a gel. The molecular weight distribution was obtained with an ionic strength of 0.085M at pH 7.2.

3. 2. IDENTIFICATION OF EFFECTIVE STABILIZERS

3.2.1 Introduction

Gum tragacanth, GT is a polysaccharide containing tragacanthic acid and arabinogalactan. In order to find which polysaccharide is responsible for the stabilization, arabinogalactan and poly (galacturonic acid) were used in the flocculation test. Poly (galacturonic acid) is a linear polysaccharide which constitutes the core of tragacanthic acid.

3.2.2 Results and Discussion

The dimensionless stability factor, W for poly (galacturonic acid) and arabinogalactan was measured as a function of polysaccharide concentrations in bulk at different pHs (Figs. 3.2. 3.3). The stabilization effect for polygalacturonic acid is much greater than that for arabinogalactan. This shows that the great stabilization effect by GT results from the linear chain of GT, i. e. ; polygalacturonic acid. The fact that high concentrations of arabinogalactan are necessary to obtain stability shows that the stability results from the change in viscosity.

Fig. 3.2 Stabilization Effect by Poly (galacturonic acid)
(PSL-1: volume fraction = 2.6×10^{-5} , MgCl_2 as flocculant, Ionic strength: 0.33M)

Fig. 3.3 Stabilization Effect by Arabinogalactan
(PSL-1: volume fraction = 2.6×10^{-5} , MgCl_2 as flocculant, Ionic strength: 0.33M)

3.2.3 Conclusions

- (1) The stabilization effect of GT results from the linear chain of poly (galacturonic acid).
- (2) The pH dependence of the amount of poly (galacturonic acid) adsorbed indicates that the binding of polygalacturonic acid is influenced by the electrostatic repulsion between segments.

3.3 EFFECT OF PRETREATMENT ON STABILITY

3.3.1 Introduction

In our preliminary studies, we found that the stabilization effect significantly depends on the pretreatment, i. e. , the pore size of filter membrane which determines the size of the GT molecules. Therefore, in order to investigate the effects of the pretreatment on the factors of steric stabilization mechanism such as steric layer thickness, zeta potential and amount of adsorbed polymers, a series of experiments were carried out using the photon correlation spectroscopy, zeta potentiometer, etc. In addition, in order to obtain the chemical structure and the molecular weight distribution of the GT samples, the FT-IR and the gel permeation chromatographic technique were employed.

3.3.2 Results and Discussion

3.3.2.1 Influence of Pretreatment on the Stabilization Effect

In order to investigate the influence of pretreatment of GT on the stabilization effect, the stability factor for GT-L (filtered through 1.20 μm pores) and GT-S (filtered through 0.22 μm pores) was measured by the turbidimetric method. The stability factor was plotted against the concentration of GT in the bulk in Fig. 3.3.

The results showed that the GT-L (filtered through 1.20 μm pores) is more effective than GT-S (filtered through 0.22 μm pores). Only 3ppm of GT-L in the bulk is sufficient to get the stability factor of 100 whereas 20 ppm of GT-S in the bulk is required to get the stability factor of 100.

Since GT is a complex mixture of acidic polysaccharides containing D-galacturonic acid, the FT-IR was carried out to observe if the chemical structure of GT samples depends on the pretreatment.

Fig. 3.3 Influence of Pretreatment on Stabilization Effect
(Dia. of latex: 330 nm, Volume fraction of latex: 2.6×10^{-5} ,
Ionic strength: 0.33 M, 293 K, pH 2.8)

3.3.2.2 FT-IR Study of GT-S (filtered through 0.22 μm pores) and GT Without Filtration

Figure 3.4 shows the FT-IR spectra for (a) GT without filtration and (b) GT-S (filtered through 0.22 μm pores). The absorptions around 2930, 1740, 1076 and 1020 cm^{-1} are assigned to the C-H stretching vibration, C=O stretching vibration, C-O stretching vibration and C-C stretching vibration, respectively. The spectra show that the wave numbers of peaks and the ratios of absorbance of peaks for GT without filtration were the same as that for the GT-S (filtered through 0.22 μm pores) although the absorbance for water was different because of the different sampling procedures (3408 cm^{-1} for OH-stretching and 1619 cm^{-1} for OH-bending). Consequently, the FT-IR spectra indicate that the chemical structure of the GT without filtration is the same as that for GT-S (filtered through 0.22 μm pores). Therefore, it was shown that the dependence of stabilization effect on the pretreatment results from rather the difference in the physical properties, such as molecular weight.

3.3.2.3 Effect of Pore Size of Membrane on the Molecular Weight Distribution

To see if there is a significant difference in the molecular weight for GT-L (filtered through 1.20 μm pores) and GT-S (filtered through 0.22 μm pores), the molecular weight distribution of GT for the different treatments was determined by GPC as given in Table 3.2.

Fig. 3.4 FTIR spectra of GT, (a) before filtration; (b) GT-S

**Table 3.2 Molecular Weight Distribution of GT samples as
determined by GPC**

Molecular weight range	Wt. %	
	GT-L	GT-S
> 600,000	46.5	25.3
600,000 - 500,000	15.5	21.7
500,000 - 170,000	18.9	27.1
170,000 - 60,000	12.8	12.5
< 60,000	6.4	13.5

The results show that the GT molecules having a molecular weight greater than 600,000 are removed by using the smaller pores, i. e. ; 0.22 μ m.

3.3.2.4 Effect of Molecular Weight on the Adsorption Isotherm

Figure 3.5 shows that the GT-L (filtered through 1.20 μ m pores) which has a greater proportion of high molecular weight fraction adsorbs on the latex surface to a greater extent than GT-S (filtered through 0.22 μ m pores).

This indicates that the larger molecules are replacing the smaller molecules on the surface of latex (12).

3.3.2.5 Influence of Molecular Weight on the Stabilization Effect

Fig. 3.5 Effect of Molecular Weight on Amount of GT adsorbed
(Dia. of latex: 330 nm, Volume fraction of latex: 2.6×10^{-3} , Ionic strength: 0.33 M, 293 K, pH 2.8)

Using the adsorption isotherms in Fig. 3.5, the stability factor was replotted against the amount of GT adsorbed as shown in Fig. 3.6.

The results show that the stability factor for GT-L (filtered through 1.20 μm pores) is much greater than that for GT-S (filtered through 0.22 μm pores) even for the same amount of GT adsorbed. In order to investigate this phenomenon, the zeta potential and the steric layer thickness were measured as a function of the amount of GT adsorbed for GT-L (filtered through 1.20 μm pores) and GT-S (filtered through 0.22 μm pores).

3.3.2.6 Effect of Molecular Weight on the Zeta Potential

To learn if the electrostatic repulsive force varies with the molecular weight distribution, the electrophoresis measurements were undertaken.

As can be shown in Figure 3.7, the comparison of zeta potential for the latex covered with the same amount of GT demonstrates that the magnitude of zeta potential is lower for GT-L (filtered through 1.20 μm pores) than GT-S (filtered through 0.22 μm pores). The decrease in the magnitude of zeta potential with higher molecular weight is probably ascribed to the fact that the shielding effect of electrolyte ions becomes significant as the steric layer thickness increases (13). This trend is consistent with the results reported by D. Heath et. al. (14). Using lignosulphonates as a polyelectrolyte, they showed that there is a reduction in the magnitude of zeta potential as the proportion of the high molecular weight fractions increases. Therefore, it was hypothesized that the steric layer thickness for GT-L (filtered through 1.20 μm pores) is greater than that for GT-S (filtered through 0.22 μm pores) at the same amount of GT adsorbed.

3.3.2.7 Effect of molecular weight on the steric layer thickness

The steric layer thickness was measured for GT-L (filtered through 1.20 μm pores) and GT-S (filtered through 0.22 μm pores) using PCS. Figure 3.8 shows that the steric

Fig. 3.6 Influence of Molecular Weight on Stabilization Effect

(Dia. of latex: 330 nm, Volume fraction of latex: 2.6×10^{-5} , Ionic strength: 0.33 M, 293 K, pH 2.8)

Fig. 3.7 Effect of Molecular Weight on Zeta Potential

(Dia. of latex: 330 nm, Volume fraction of latex: 2.6×10^{-5} , Ionic strength: 0.33 M, pH 2.8)

Fig. 3.8 Effect of Molecular Weight on Steric Layer Thickness
(Dia. of latex: 330 nm, Volume fraction of latex: 9.4×10^{-7} , Ionic strength: 0.085 M, 293 K, pH 3.4)

layer thickness for GT-L (filtered through 1.20 μm pores) is greater than that for GT-S (filtered through 0.22 μm pores) with the same amount of GT adsorbed.

Therefore, the greater stabilization effect for the GT having greater proportion of high molecular weight fraction can be attributed to the greater steric layer thickness. The greater steric layer thickness for GT-L (filtered through 1.20 μm pores) was also indicated by the calculation of the projected area for one GT molecule as follows (Table 3.3).

Table 3.3 Effect of molecular size on stability

	PORE SIZE	M _w	AMOUNT OF ADSORPTION	THICKNESS	W(3ppm)
	[μm]		[mg/m ²]	[nm]	
GT-L	1.2	7.7×10^5	0.6	110nm	100
GT-S	0.22	5.6×10^5	0.25	70	3

For larger molecules, the projected area for one molecule is smaller than smaller molecules. Therefore, for larger molecules, they have to stand up, giving a greater thickness.

[Calculation]

GT-S (filtered through 0.22 μm pores)

0.25mg/m²

$[0.25 \times 10^{-3} / (560000)] (6.02 \times 10^{23}) / (10^9)^2 = 1 \text{ GT molecule} / 3700 \text{ nm}^2$.

GT-L (filtered through 1.20 μm pores)

0.60mg/m²

$$[0.60 \times 10^{-3} / (770000)] (6.02 \times 10^{-23}) / (10^9)^2 = 1 \text{ GT molecule} / 2100 \text{ nm}^2.$$

3.3.3 Conclusions

- (1) The molecular weight distribution was found to be changed by the membrane filtration although the chemical structures were identical for the different range of molecular weight distribution.
- (2) The adsorption isotherms showed that the GT having a greater proportion of higher molecular weight fraction adsorbs on the latex spheres to a greater extent than the GT having smaller molecular weight.
- (3) The magnitude of zeta potential was found to be lower for the GT having a greater proportion of higher molecular weight because of the shielding effect of electrolyte ions.
- (4) The steric layer thickness was greater for the GT having a greater proportion of higher molecular weight with the same amount of GT adsorbed. Because of greater steric layer thickness, the stability was higher for the GT having a greater proportion of higher molecular weight fraction.

3.4 EFFECT OF pH ON STABILITY

3.4.1 Introduction

Our preliminary studies indicated that the stability can be controlled by the solution pH. In order to find the effects of pH on stability, the amount of adsorption, zeta potential, steric layer thickness were measured as a function of pH.

3.4.2 Results and Discussion

3.4.2.1 Effect of pH on the Stability Factor

The dimensionless stability factor, W , was measured as a function of GT concentration for different pH solutions. Figure 3.9 shows that the stability increases greatly as the pH decreases.

To find the degree of dissociation of carboxylic acid in GT at various pH and to study the proton-dissociation behavior of GT, the values for pK_a and n were measured at the same ionic strength used in flocculation measurements. The value for n represents the interaction between COO^- groups in one GT molecule in Henderson-Hasselbach equation (Eq. [3]).

$$pH = pK_a + n \log \{a / (1-a)\} \quad [3]$$

where;

a : degree of dissociation

pK_a : apparent value of pK

n : constant for interaction of COO^- groups

The results were shown in Table 3.4.

Fig. 3.9 Effect of pH on Stabilization by GT
(0.33 μm -Latex: volume fraction = 2.6×10^{-5} , MgCl_2 as Flocculant, Ionic Strength:
0.33 M)

Table 3.4 pKa and n for GT and Poly (galacturonic acid)

	pKa	n
GT	3.0	1.5
Poly (galacturonic acid)	2.9	1.5

The pKa for GT was found to be 3.0 and corresponds to an apparent degree of dissociation, $\alpha = 0.5$. This pKa value is comparable to that for poly (galacturonic acid), which was found to be 2.9. The value for n of GT is also the same as that of poly (galacturonic acid) to be 1.5. Consequently one can consider that proton-dissociation behavior of GT is the same as that of poly (galacturonic acid). This similar proton-dissociation behavior of GT and PGUA can also be suggested by the similar effect of pH on the stability for PGUA as has been shown in Fig. 3.2.

There are three main possibilities for the variation in the dimensionless stability factor with pH at the same concentration of GT in bulk: (A) the amount of GT adsorbed on particles varies with pH at the same concentration of GT in bulk, (B) the electrostatic repulsive force varies with pH, or (C) the conformation or steric layer thickness is altered by changing pH. To examine these possibilities, the adsorption isotherms and the zeta potentials were determined, and PCS measurements were carried out.

3.4.2.2 Adsorption Isotherms of GT on Latex as a Function of Solution pH

To examine the effect of pH on the amount of GT adsorbed, the adsorption isotherms were determined as a function of pH at various ionic strengths. Figures 3.10, 3.11 shows that pH has little effect on adsorption isotherms when the ionic strength is higher than 0.085M. Since electrostatic interactions among polyelectrolytes (inter-chain

Fig. 3.10 Adsorption Isotherms at Ionic Strength of 0.01 M and 0.06 M

Fig. 3.11 Adsorption Isotherms at Ionic Strength of 0.085 M and 0.5 M

interactions) on the surface of adsorbent are known to affect the amount of adsorption (15), this insensitivity of the amount of adsorption to pH variation indicates that the contribution of electrostatic interactions among polyelectrolytes to the adsorption is not significant at the ionic strengths greater than 0.085M.

On the other hand, the adsorption isotherms at the ionic strengths of 0.01M and 0.060M show that the amount of adsorption depends significantly both on pH and the ionic strength, indicating that the variation of the electrostatic interaction with pH affects the amount of adsorption at the low ionic strength.

Our results differ from the results obtained by Cosgrove, et. al. (16) who showed that for the system of negative poly (styrene sulphonate) adsorbing on negative polystyrene latex particles, the adsorbed amount of polyelectrolyte increases with increasing ionic strength up to $\sim 1\text{M NaCl}$. This difference is due to the fact that the main driving force for the adsorption is not only the electrostatic force, but also the hydrophobic interactions due to the esterified carboxyl groups in GT as shown in Fig. 1.1 (17). The insensitivity of the adsorbed amount to the ionic strength was also noted for the hydrophobic adsorption of proteins (18). In order to find the effect of hydrophobicity of adsorbent on the adsorption of GT, the latex spheres with different hydrophobicity with the same diameter ($0.30\mu\text{m}$) were employed for the binding study of GT. Figure 3.12 shows that more GT binds to the hydrophobic latex.

Thus, the surface hydrophobicity was found to contribute significantly to the adsorption of GT.

3.4.2.3. Effect of pH on the Electrostatic Repulsion Force

To learn if the electrostatic repulsive force between particles varies with pH, electrophoresis measurements were undertaken. Figure 3.13 shows the zeta potential is virtually independent of pH when the latex particles are covered with the same amount of GT (0.25 mg/m^2).

Fig. 3.12 Effect of Hydrophobicity of Latex on Adsorption of GT
(pH 7.4, Ionic strength: 0.085 M, Volume fraction of latex: 3.1×10^{-3})

Fig. 3.13 Effect of pH on Zeta Potential

(Amount of GT adsorbed: 0.25 mg/m^2 , Ionic strength: 0.33 M)

The ionic strength was 0.33M which corresponds to the value after the addition of magnesium chloride. This relative insensitivity of the zeta potential to pH variation probably results from the high ionic strength and the suppression of electrostatic interactions.

Therefore, it was found that the variation in the dimensionless stability factor with pH is not due to the difference in the electrostatic repulsive force between particles.

3.4.2.4. The effect of pH on the steric layer thickness

The polystyrene latex spheres with a volume fraction of 9.4×10^{-7} were incubated for 1 day in the GT solution (107ppm). This concentration of GT corresponds to the saturation point of adsorption isotherms where the amount of GT adsorbed on the latex is 0.25 mg/m^2 . The particle diameter was then measured by PCS at an ionic strength of 0.085M as shown in Fig. 3.14.

Figure 3.14 shows that the steric layer thickness is greater in solutions with a lower pH. Since the solution contains GT molecules with highly polydisperse molecular weight, the following experiment was performed to see if the difference of thicknesses with pH is due to the difference of molecular size adsorbed or the difference of conformation. After the latex particles were incubated in the GT solution (107ppm GT, pH 7.4, ionic strength: 0.085M, 293K), the solution was centrifuged, and the supernatant with GT was decanted. The equivalent amount of buffer solution (pH 7.4) was then added. After the ultrasonication to redisperse the particles at the bottom of the centrifuge tube, the pH was lowered to pH 2.8 by adding 0.085M-HCl, and the particle thickness was measured by PCS. The PCS data showed that the thickness increased from 16nm to 70nm in about 40 minutes. If the molecules of different sizes were adsorbed at different pH, this would not be observed. This indicates that the difference of the thickness with pH is due to the difference of the conformation of GT molecules. At a lower pH, the ionization of

Fig. 3.14 Effect of pH on the Conformation of GT
(Ionic strength: 0.085 M, 293K)

carboxylic groups is repressed so that GT molecules behave like uncharged polymers, and they form loops or tails. On the other hand, at a higher pH, since GT molecules are charged to a greater extent, the formation of loops and tails is suppressed because of strong intra-chain interactions. The similar phenomena was observed by Chandar, et. al. (19) whose excimer fluorescence study showed that poly (acrylic acid) adsorbed on alumina takes a coiled form at a lower pH.

The greater value for the radius of gyration at a high pH (Fig. 3.14) shows that the GT molecules expand in the solution at a high pH because of strong intra-chain interactions. This expansion of GT molecules at a high pH is also suggested by the viscosity data obtained by Byrum, et. al (20) as listed in Table 3.5. They showed that the viscosity of the 1% w/v solution with the GT increases as the pH increases.

**Table 3.5 Influence of pH on viscosity of the GT solution
(1M-NaOH / 1M-HCl)**

pH	Viscosity at 30°C [cP]
3	5.4
5	6.5
7	13.3

These results are schematically summarized in Fig. 3.15.

The significant variation of the thickness with pH compared to the insensitivity of the amount of adsorption to pH indicates that the thickness is determined mainly by the tails,

	In Solution	On Surface
Low pH	 Small R_g	 Large thickness
High pH	 Large R_g	 Small thickness

Fig. 3.15 Conformation of GT in solution and on the surface

the volume fraction of which is relatively small (21). These tails belong to the main linear chains of 1, 4 linked α -D-galacturonic acid since the branches are too short to give the thickness in the order of 10 nm.

These results demonstrate that the difference in the dimensionless stability factor with various pH at the same amount of GT adsorbed is due to the difference in the steric layer thickness. In other words, the greater stability at a low pH is due to the greater steric repulsion.

It should be noted here that the effect of adsorbed polymers on the hydrodynamic correction factor is not significant as described below. The Einstein relation for the diffusion coefficient and the Stokes expression for viscous drag on a sphere both apply strictly only to single spheres in a medium of infinite extent. When two spheres are close together, their diffusion can no longer be described by simply setting $D_2 = D_1 + D_1$ (D_2 : diffusion coefficient for two spheres, D_1 : diffusion coefficient for one sphere). Instead, D_2 is substantially smaller. When the hydrodynamic effect is included, D_2 goes to 0 as the particles approaches. This absurdity is easily resolved by taking into account the van der Waals dispersion forces. The hydrodynamic effect predicts it to be slower by roughly 50% than the coagulation rate without the hydrodynamic correction (22). This ratio depends on the value of Hamaker constant. However, in the presence of adsorbed water-soluble polymers, there is no significant change in Hamaker constant. Therefore, the effect of polymer on the hydrodynamic correction is negligible.

3.4.2.5 Deflocculation

In order to observe if the polystyrene latex spheres which have flocculated at higher pH can be redispersed by changing the conformation of GT, the pH of the solution was lowered. GT (29.7ppm) was added to the buffer solution (pH 7.4) with latex spheres of the volume fraction of 2.6×10^{-5} . After 1 day incubation, magnesium chloride was added, and the turbidity was measured by the spectrophotometer. The turbidity increased as the

particles flocculated and then reached a constant value after 65 minutes. Next, the pH was then changed from 6.2 (the pH dropped from 7.4 to 6.2 after the addition of magnesium chloride.) to 2.8 by adding hydrochloric acid solution of the same ionic strength of the latex solution (0.33M) and gently mixing the solution. The turbidity decreased after the addition of acid as shown in Fig. 3.16, indicating that the aggregates were deflocculated. ΔT and T_0 represent the difference in turbidity and the initial turbidity, respectively.

In order to find if this flocculation-deflocculation process is reversible the following experiments were performed. GT (107 ppm) was added to the buffer solution (pH 7.4) with latex spheres of the volume fraction of 2.6×10^{-5} . After the 1 day incubation, the salt was added to induce flocculation. As shown in Fig. 3.17, the turbidity increased linearly with time due to the doublets formation. Then, the pH was changed to pH 2.8. The turbidity decreased to the initial value showing that the doublets were deflocculated, and Fig. 3.17 shows that this flocculation-deflocculation process can be repeated back and forth.

To substantiate that the increase in the steric layer thickness causes the deflocculation, PCS study was undertaken. After the latex spheres were incubated with 107 ppm of GT at pH 6.2 for 1 day at 293K, hydrochloric acid solution was added to lower the pH to 2.8. It should be mentioned that for PCS study the salt was not added further because the thickness could not be determined in the presence of aggregates. Figure 3.18 shows that the steric layer thickness increases from 20 nm to 65 nm approximately 40 minutes after the pH was lowered, indicating that it required ca. 40 minutes for GT molecules to change the conformation.

It should be noted here that the time required for the diffusion of the hydrochloric acid into the adsorbed layer is negligible by three orders of magnitude compared to the 40 minutes required for this conformational change. Consequently, the deflocculation is attributed to the change in the conformation of GT with the decrease in pH. The cause of

Fig. 3.16 Effect of Change of pH on the Stability

Fig. 3.17 Flocculation - Deflocculation

Fig. 3.18 The Change of Thickness with Time

the difference between the magnitude of the time constant for the deflocculation (100 minutes) and the magnitude of the time constant for the conformational change (20 minutes) is open to speculation. Since the flocculation studies showed that for pH 2.8 the flocculation is negligible for the same amount of GT adsorbed as pH 6.2, it is possible that the time for the deflocculation (5 hours) corresponds to the time required for the conformation to change completely for the aggregates. The van der Waals attraction force between the particles or the strong interactions of polymers attaches to the different particles presumably make the conformational change difficult in case of aggregates as shown in Fig. 3.19.

Fig. 3.19 Deflocculation Mechanism

3.4.3 Conclusions

- (1) The stability can be controlled by changing pH.
- (2) At high ionic strength, the amount of GT adsorbed does not change with pH.
However, as the pH is lowered the steric layer thickness expands from 16 nm to 70 nm. This suggests that GT changes conformation on the surface and that this conformational change is a result of the formation of loops and tails at the lower pH.
- (3) The flocculated particles can be spontaneously deflocculated by lowering pH. The peptization is a result of the conformational change of the GT molecules on the surface, and the flocculation-deflocculation process is reversible.
- (4) The binding mechanism of GT is influenced by the hydrophobic nature of the adsorbent.

3.5 EFFECT OF NATURE OF ELECTROSTATIC INTERACTIONS ON THE STABILITY

3.5.1 Introduction

Our studies of gum tragacanth (an acidic polysaccharide based on galacturonic acid) showed that colloidal stability can be controlled by the solution pH (23). This change of the stability with pH was found to be due to the conformational change of gum tragacanth adsorbed on the surface caused by the protonation of the carboxyl groups of gum tragacanth.

In order to investigate how this conformational change of polysaccharides on the surface is influenced by the adsorption affinity between the surface and poly (galacturonic acid), PGUA, positively charged amidine polystyrene latices were used as well as negatively charged sulfate polystyrene latices. The PGUA is a well defined linear homopolysaccharide which corresponds to the main chain of gum tragacanth. Since the PGUA is negatively charged due to the deprotonation of carboxyl groups ($pK_a = 2.9$), the adsorption affinity would be enhanced when the particles are positively charged as in the case for amidine particles due to the electrostatic attraction force. The flocculation rate, the amount of adsorption, and the steric layer thickness were measured at pH 2.0, pH 3.8 and pH 8.2 which correspond to the degree of dissociation of carboxyl groups of 0.2, 0.8 and 1.0, respectively. The results with the amidine latices were compared with the results with the sulfate latices. In addition, the peptization process for the amidine latices and the sulfate latices was examined.

3.5.2 Results and Discussion

3.5.2.1 Monodispersed PGUA

In order to obtain the monodisperse PGUA, the gel permeation chromatography, GPC was carried out. The elution profiles were obtained before and after the fractionation with the ionic strength of 0.05M at pH 8.2. The results are shown in Figs. 3.20 and 3.21 (V_o : void volume, V_t : total bed volume). The fraction which has the molecular weight of 540,000 and the polydispersity of 1.08 was used for the flocculation test and the adsorption study.

3. 5.2.2 Effect of Electrostatic Interactions on the Amount of Adsorption

Figure 3.22 shows that [1] more PGUA adsorbs on the positive surface than on the negative surface and that [2] the higher pH value gives a smaller amount of adsorption both for the positively and the negatively charged latices. The greater amount of adsorption for the positive surface ([1]) is due to the strong electrostatic attraction between the positively charged latices and the negatively charged PGUA. The conformational change with pH was suggested by the dependency of adsorption on pH for both the positive and negative surfaces ([2]). The smaller amount of adsorption at the higher pH, both for the positively and the negatively charged latices, indicates the significant intrachain repulsion at the high pH which gives a flat configuration. The effect of the intrachain repulsion on adsorption was also studied by Cosgrove, et. al. (24) who showed that negatively charged poly (styrene sulfonate) adsorbs less on a positively charged surface at lower ionic strength due to the flat configuration. When the amount of charge in PGUA increases with the increase of pH,

Fig. 3.20 Elution Profile of PGUA before fractionation

Fig. 3.21 Elution Profile of PGUA after fractionation

Fig. 3.22 Effect of the Electrostatic Interactions on the Adsorption

the strong electrostatic repulsion between the segments makes it difficult for the adsorbed polyelectrolytes to take loops or tails. Therefore, the adsorbed layer becomes flat, and the amount of adsorption becomes smaller at the high pH.

3.5.2.3 Effect of Electrostatic Interactions on the Steric Layer Thickness

In order to substantiate the conformational change of adsorbed PGUA with pH indicated in Fig. 3.22, the steric layer thickness was measured by the photon correlation spectroscopy. The concentration of PGUA in the supernatant was 32.7ppm which corresponds to the saturation point. Figure 3.23 shows that [1] the steric layer thickness for the high pH is smaller than that for the low pH, and that [2] the negative surface gives comparable thicknesses to the positive surface at the same pH even though the amount of adsorption is smaller than that for the positive surface. This means that the smaller steric layer thickness at higher pH ([1]) is believed to be due to a flat conformation of PGUA on the surface resulting from stretching of PGUA molecules having a greater number of charged groups. In order to substantiate this, the conformation of PGUA molecules in the solution, i. e., the radius of gyration, was measured as a function of pH. Figure 3.24 shows that the PGUA molecules are stretched out at higher pH. These stretched molecules give a flat conformation on the surface. The smaller steric layer thickness compared to the radius of gyration suggests that most semiflexible rod-like PGUA molecules are laid on the surface.

The comparable thickness for the negative surface to that for the positive surface at the same pH ([2]) results from the strong electrostatic attraction between the positively charged particles and the negatively charged PGUA. The PGUA adsorbed on the positively charged surface tends to take a flatter conformation than that on the negatively charged surface as shown in Fig. 3.25.

Fig. 3.23 Steric Layer Thickness for Amidine and Sulfate Latices

Fig. 3.24 Effect of pH on Rg

Fig. 3.25 Effect of Electrostatic Interactions on Conformation

Latex	On Surface
Sulfate	Large thickness
Amidine	Small thickness

3.5.2.4 Effect of Electrostatic Interactions on the Stability

In order to study the effect of the steric layer thickness on the stability, the stability factor, Eq. [1], was determined by the turbidimetric measurement (10). The concentration of PGUA after the adsorption was 32.7 ppm which corresponds to the saturation point. Figure 3.26 shows that the PGUA can stabilize the negative particles more efficiently than the positive particles at the same pH. This might be due to the slightly greater steric layer thickness for the sulfate latices than the amidine latices at the same pH. The greater thickness gives greater stability because of the steric repulsion. This steric repulsion results from the mixing free energy change and the elastic free energy change (25).

3.5.2.5 Effect of the Adsorbed PGUA on the Zeta Potential

The stability results indicated that the stabilization is mainly due to a steric repulsion. In order to study the effect of the electrostatic repulsive force on the stability, the zeta potential was measured for both the amidine latices and the sulfate latices as a function of the solution pH in the presence and the absence of PGUA (32.7 ppm). The ionic strength was 0.33 M which corresponds to the ionic strength after the addition of the sodium chloride for the flocculation test.

Figures 3.27 and 3.28 show that both for the amidine latices and for the sulfate latices the magnitude of the zeta potential in the presence of PGUA is less than 10 mV. It should be noted that in the absence of PGUA the ionic strength of 0.33 M corresponds to a rapid flocculation region where there is no effect of electrostatic repulsion on the flocculation rate. The zeta potential in this rapid flocculation region is +13 mV for the amidine latices, and -10 mV for the sulfate latices. Therefore, the effect of electrostatic repulsion would not be

Fig. 3.26 Stability of Amidine and Sulfate Latices

Fig. 3.27 Effect of pH on Zeta Potential of Amidine Latices

Fig. 3.28 Effect of pH on Zeta Potential of Sulfate Latices

significant unless the magnitude of zeta potential is much greater than these values for the rapid flocculation.

The fact that PGUA has no significant effect on the electrostatic repulsive force substantiated that the effect of pH on the stability is not due to the change in the electrostatic repulsive forces.

The decrease in the zeta potential at lower pH for the PGUA-covered amidine latices is due to the fact that the slipping plane is located further away from the surface than at higher pH. This location of the slipping plane for lower pH had been suggested by the greater steric layer thickness for lower pH. The shift in the slipping plane outwards as a result of the extension of the steric layer has been investigated by Heath, et. al. (14) who suggest that the exponential drop in the potential as a function of the distance between the surface and the slipping plane suppresses the electrical potential at the slipping plane.

No change in the zeta potential for the sulfate latices in the presence of PGUA is due to the smaller amount of adsorption which leads to a smaller amount of charge in the adsorbed layer.

3.5.2.6 Effect of Electrostatic Interactions on Peptization

After the latices covered with gum tragacanth were flocculated at a high pH, a subsequent drop of the pH peptized the aggregates. The peptization is due to the expansion of GT molecules on the surface of sulfate latices. In order to observe how the electrostatic interactions between the particle and the polysaccharides influence this peptization, both the amidine latices and the sulfate latices were used in the peptization study. The PGUA (32.7ppm) was added to the buffer solution (pH 8.2) with latex spheres of the volume fraction of 2.6×10^{-5} . After 2 hours incubation, sodium chloride was added, and the turbidity was measured using the spectrophotometer. The turbidity increased linearly with time as the particles flocculated into doublets. This linearity would not be observed if the

triplets or larger aggregates begin to form (26). During the time when only doublets are forming, the pH was changed from 8.2 to 2.0 by adding hydrochloric acid solution of the same ionic strength of the latex solution (0.33M) and gently mixing the solution. The turbidity for the sulfate latices decreased after the addition of acid as shown in Fig. 3.29. The change in turbidity and the initial turbidity are expressed as ΔT and T_0 , respectively. This change in the turbidity shows that the sulfate doublets were immediately peptized into singlets. On the other hand, the turbidity for the amidine latices remained constant, showing that the doublets could not be peptized even after 3 hour.

These results indicate that the conformational change with lowering the pH is strongly influenced by the electrostatic interactions between the particle and the polyelectrolytes. In case of the amidine latices, the adsorption is stronger than the case for the sulfate latices since the particle is positively charged and the PGUA is negatively charged. Therefore, the conformational change is not favorable as shown schematically in Fig. 3.30.

To substantiate that the increase in the steric layer thickness causes the peptization of the sulfate latices, PCS measurements of the steric layer thickness were carried out. After the sulfate latices were incubated with 32.7 ppm of PGUA at pH 8.2 for 2 hours at 293K, hydrochloric acid solution was added to lower the pH to 2.0. Figure 3.31 shows that the steric layer thickness increased from 6 nm to 20 nm approximately 3 minutes after the pH was lowered. The increase of the steric layer thickness of the sulfate latices indicated that the formation of loops and tails accompanied by the decrease in the solution pH caused the peptization of the particles which had flocculated at higher pH.

On the other hand, the steric layer thickness of the PGUA adsorbed on the amidine latices remained constant over several hours after the drop of the pH.

Fig. 3.29 Effect of pH drop on Peptization for AL and SL

Fig. 3.30 Effect of Electrostatic Interactions on Conformational Change

Fig. 3.31 Change of Steric Layer Thickness of SL after the decrease in pH

3.5.2.7 Peptization of Sulfate Latices

In order to study the peptization mechanism of sulfate latices, the turbidity data were analyzed using the optical factor calculated from the Mie theory. Before the addition of salt, the latices are all singlets. Therefore,

$$\tau_{\text{initial}} = C_1 N_{\text{initial}}$$

where τ_{initial} = turbidity before addition of salt,
 C_1 = optical factor for singlets [m^3],
 N_{initial} = particle concentration of singlets before the addition of salt [m^{-3}].

After the addition of salt, initially the turbidity increases linearly with time showing that only doublets are formed (26). However, after the initial flocculation of singlets, triplets or quartets begin to form, and the turbidity-time curve becomes nonlinear. During the time when only doublets are forming, the turbidity is expressed as

$$\begin{aligned}\tau_0 &= C_1 N_{10} + C_2 N_{20} \\ &= C_1 (N_{\text{initial}} - 2 N_{20}) + C_2 N_{20}\end{aligned}$$

where τ_0 = turbidity when the acid is added,
 N_{10} = particle concentration of singlets when the acid is added [m^{-3}],
 N_{20} = particle concentration of doublets when the acid is added [m^{-3}].

If it is assumed that the peptization rate of doublets is proportional to the particle concentration of doublets, the peptization rate is expressed as

$$dN_2/dt = -P N_2 \quad [3]$$

where P = peptization rate constant [min^{-1}],
 N_2 = particle concentration of doublets at time t .

From Eq. [3],

$$N_2 = N_{20} \exp(-P t)$$

The particle concentration of singlets N_1 at time t is expressed as

$$N_1 = N_{10} + 2(N_{20} - N_2)$$

Therefore, the turbidity at time t is

$$\begin{aligned} \tau &= C_1 N_1 + C_2 N_2 \\ &= C_1 (N_{10} + 2 N_{20}) + (C_2 - 2 C_1) N_{20} \exp(-P t) \\ \ln (\tau - C_1 (N_{10} + 2 N_{20})) &= (-P) t + \text{constant} \end{aligned}$$

The slope of $\ln (\tau - C_1 (N_{10} + 2 N_{20}))$ vs. t curve gives the peptization rate constant.

Therefore, when the peptization rate is proportional to the particle concentration of doublets, a plot of $\ln (\tau - C_1 (N_{10} + 2 N_{20}))$ as a function of time is linear. As shown in Fig. 3.32, a linear relation was observed except the initial point where there is a dead time resulting from the time for the conformational change to occur. Therefore, it was found that the peptization rate is proportional to the particle concentration of doublets. This is due to the spontaneous nature of the peptization. The peptization rate constant was calculated to be $0.15 [\text{minute}^{-1}]$, i. e.,

$$dN_2/dt = -0.15 N_2$$

Fig. 3.32 Determination of Peptization Rate Constant

3.5.3 Conclusions

- (1) The electrostatic interactions between the particles and the polysaccharide have a significant effect on the stability, the amount of adsorption and the steric layer thickness. The electrostatic repulsion between the negatively charged particles and the negatively charged polysaccharide gives a comparable thickness to the case of the positively charged particles at the same pH.
- (2) Lowering the pH caused the immediate peptization of the sulfate latices while the amidine latices were not peptized even after 3 hour. This is due to the fact that the strong binding of PGUA with the positive surface makes a conformational change difficult to take place.
- (3) The peptization of doublets for the sulfate latices could be represented by the model in which the peptization rate is proportional to the particle concentration of doublets.

3.6 DIRECT FORCE MEASUREMENTS BETWEEN POLYSACCHARIDE-BEARING MICA SURFACES

3.6.1 Introduction

Our previous studies have shown that colloidal particles can be sterically stabilized by adsorbed acidic polysaccharides such as gum tragacanth, GT and poly (galacturonic acid), PGUA (1, 2, 3). In order to directly observe steric repulsive forces between two surfaces, the forces between atomically smooth mica sheets bearing the acidic polysaccharides were measured using the Surface Force Apparatus designed by Israelachvili and Adams (27). In addition, the steric layer thickness measured by photon correlation spectroscopy, PCS was compared with the thickness at which forces begin to arise. This comparison is essential because [1] Tadros (28) indicated in his rheological experiments that the steric layer thickness measurements by PCS tend to underestimate the thickness at which forces begin to arise and [2] our interpretation of effects of pH, molecular weight and surface charge on stability is based on the steric layer thickness measured by PCS.

The GT sample used was polydisperse (weight average molecular weight, M_w = 560,000, polydispersity index = 2.7) whereas the PGUA sample was monodisperse (M_w = 540,000, polydispersity index = 1.08). To our knowledge, this is the first attempt to measure the force profiles using a well-defined homopolysaccharide, PGUA.

3.6.2 EXPERIMENTAL

3.6.2.1 Materials

All chemicals and solvents were analytical grade materials. The water used for washing and preparation of aqueous electrolyte solutions was deionized. All liquids were filtered through 0.22 μ m Millipore filters before they were introduced into the cell.

3.6.2.2 Apparatus

The Surface Force Apparatus is shown schematically in Fig. 3.33. Muscovite mica is cleaved to provide thin (~ 2 μ m) sheets that are molecularly smooth on both sides, and these mica sheets can be used as substrates in studying surface forces. Two smooth curved mica sheets are glued on cylindrical lenses using epoxy glue and mounted opposite to each other in a crossed cylindrical configuration. The top sheet is rigidly mounted on a piezoelectric crystal whereas the bottom surface is mounted on the rigid movable arm via a flexible leaf spring. The distance between the surfaces is measured by an optical method involving multiple beam white-light interferometry (29). The forces between the surfaces are measured from the difference of applied displacement and actual displacement. Finally, the mean radius of curvature of the cylindrically curved mica surfaces near the contact area can be calculated from the shape of the interference fringes.

3.6.2.3 Procedure

Prior to experiments, all parts of the apparatus were thoroughly cleaned and dried (glass parts by standing in sulfuric acid overnight, metal parts in dilute acid, and all parts finally rinsed in filtered ethanol and dried in a laminar flow cabinet). The apparatus was

Fig. 3.33 Surface Force Apparatus

then assembled, closed and mounted in a vibration-free, thermally insulated box. The mica surfaces were brought to contact in air, and the optical parameters of the system were noted. Next, a 0.1 M-KCl solution was added to the cell, and the forces were measured in the absence of polysaccharides. A high ionic strength of 0.1 M was used to suppress the double layer for the negatively charged mica and the negatively charged polysaccharides and to obtain a sufficient amount of adsorption. The polysaccharide was then added to the required concentration, and the surfaces were allowed to incubate in the solution at a separation distance of 2 mm in order to permit adsorption to take place. The forces were then again measured.

3.6.3 Results and Discussion

The force/distance profiles presented in the following sections are plotted as F/R vs. D (F : force, R : radius of curvature, D : separation distance). The force axis was normalized by dividing the force by the mean radius R of the mica sheets. In the Derjaguin approximation (30),

$$F/R = 2\pi V_{\text{plate}} \quad [1]$$

where V_{plate} is the interaction energy per unit surface area between two flat parallel plates. Therefore, the effect of the curvature of different mica surfaces in the different experiments was eliminated.

3.6.3.1 Force Profiles of Gum Tragacanth

The force/distance profiles are shown for a 0.1 M-KCl solution and for a GT solution (15.5 $\mu\text{g/ml}$) in a 0.1 M-KCl solution in Fig. 3.34. The solution pH was adjusted to pH 2.9 by adding HCl. The force profile for the 0.1 M-KCl solution shows that the repulsive force decreases exponentially with increasing distance according to the decay of the

electrical double layer repulsion (31, 32). The decay length (1.8 nm) was reasonably close to the theoretical one (0.95 nm).

Fig. 3.34 Force Profiles for GT (pH 2.9, 15.5 µg/ml, 301 K)

The decay length, κ^{-1} is expressed in Eq. [2].

$$F \sim \exp(-\kappa D) \quad [2]$$

The decay lengths for the force profiles are listed in Table 3.6. In the solution with a high electrolyte concentration (0.1M-KCl), there is no background double-layer repulsion for $D > 20$ nm. Therefore, any observed repulsion for $D > 20$ nm is entirely due to the GT molecules adsorbed on the mica surfaces.

To compare the van der Waals force between two surfaces with other forces, the van der Waals attraction forces were plotted in Fig. 3.34, using the following equation.

$$F/R = -A / (6 D^2) \quad [3]$$

A : Hamaker constant ($= 2.2 \times 10^{-20}$ J).

This equation was obtained by Israelachvili et. al. using calculated values for electrical repulsive forces and observed forces (33). The Hamaker constant was approximated to be that for mica in water since the presence of water-soluble polymers on the surface has no significant effect on the overall Hamaker constant (34). Figure 3.34 shows that the van der Waals force becomes negligible as $D > 10$ nm.

The force profile for GT in a 0.1 M-KCl was independent of the incubation time after 16 hours at 301 K. Measurements were started at a large surface separation ($D = 300$ nm). No forces were detected down to $D = 140$ nm, where an exponentially increasing force was observed. The decay length for the surfaces with GT was much greater than that for the surfaces without GT, indicating that the adsorbed GT molecules give a steric repulsion, not an electrostatic repulsion which was found to be operative for polyelectrolytes such as poly-L-lysine (35).

Table 3.6 Decay Length of Force Profiles

Decay Length [nm]	
0.1 M - KCl only	1.8 (0.95 ^a)
GT (pH 2.9)	32.0
PGUA (pH 2.0)	17.2

^a From the DLVO theory

The steric layer thickness δ is half the value of D at which onset of repulsion is first observed. The value of δ is thus 70 nm, a value comparable to that obtained for the steric layer thickness of GT adsorbed on latex particles from PCS (36). The steric layer thickness was found to be smaller than $2R_g$ (≈ 110 nm) indicating that the GT molecules are adsorbed with multiple points attached to the surface whereas di-block copolymers are known to be stretched out on the surface due to a terminal attachment ($\delta > 2R_g$) (37).

The force profile of GT shows only repulsive forces, confirming the fact that the aqueous electrolyte solution is a good solvent in which mutual polymer segment interactions are thermodynamically unfavorable (38). If the solvent is a worse solvent, a potential energy well would appear due to the mutual attraction of the segments although a steep repulsion would be observed on a closer approach due to an elastic repulsion. An important feature in interpreting the results is the irreversible adsorption of GT. As the adsorbed layers come into overlap with no desorption, the effective segment concentration in the gap increases with consequent increasing osmotic repulsion.

On decompression immediate after the compression, hysteresis was observed. The effect of decompression on the force profile, which is to reduce the repulsive force for a given D , can be explained as follows. On compression, more polymer segments were

forced onto the mica surface, and did not have time to move off the surfaces during decompression.

3.6.3.2 Force Profiles of Poly (galacturonic acid)

The force/distance profiles are shown for a 0.1 M-KCl solution and a PGUA solution (7.7 $\mu\text{g/ml}$) in Figs. 3.35 and 3.36. The solution pH was adjusted to pH 2.0 by adding HCl. The force profile for PGUA in a 0.1 M-KCl was independent of the incubation time after 8 hours at 303 K as shown in Fig. 3.35. Measurements were started at a large surface separation ($D = 300$ nm). No forces were detected down to $D = 70$ nm. However, below 70 nm, exponentially increasing forces were observed. GT gave a larger thickness than PGUA although the average molecular weight is similar. This is due to the polydispersity of GT: the area of mica is so small (~ 1 cm²) that largest molecules adsorb on the mica. The decay length for the surfaces with PGUA was much greater than that for surfaces without PGUA, indicating that PGUA molecules give a steric repulsion, not an electrostatic repulsion. The steric layer thickness is 35 nm, a value comparable to the steric layer thickness of 18 nm obtained by PCS (39). This slight difference in the steric layer thickness obtained by the Surface Force Apparatus and PCS might be due to the fact that PCS does not detect long - dangling tails of the PGUA molecules (28). The steric layer thickness was found to be smaller than $2R_g$ (≈ 50 nm) indicating that the PGUA molecules are adsorbed with multiple points attached to the surface. Force profile of PGUA shows only repulsive forces which confirm the fact that an aqueous electrolyte solution is a good solvent for PGUA.

Fig. 3.35 Force Profiles for PGUA (pH 2.0, 7.7 µg/ml, 303K)
Equilibrium adsorption after 8 hours incubation

Fig. 3.36 Force Profiles for PGUA (pH 2.0, 7.7 $\mu\text{g/ml}$, 303 K)

On decompression immediate after the compression, hysteresis was observed. The flattened PGUA molecules were found to relax to the original compression curve after 30 minutes (the second compression in Fig. 3.36).

3.6.3.3 Stabilization Mechanism

The force profiles for the mica sheets can be used to obtain force profiles for two spheres and to elucidate the mechanism of the stabilization of colloidal particles by the acidic polysaccharides.

The force profiles for two spheres can be estimated using the Derjaguin approximation (31). From the Derjaguin approximation,

$$V_{\text{sphere}} = (\pi a / \kappa) V_{\text{plate}}$$

V_{sphere} : interaction energy between two spheres

a : particle radius

Combining this with Eq. [1],

$$V_{\text{sphere}} = (a/2\kappa) (F/R)$$

Using this equation, force profiles for two spheres can be calculated from the force profiles for the mica sheets. The van der Waals force for the spheres covered with polymers can be calculated using Eq. [4] derived by Vincent (40).

Fig. 3.37 Flocculated Doublet ($d \approx 2h$)

$$V_A = - (1/12) [(A_2^{1/2} - A_3^{1/2})^2 (a + h) / (a - 2h) + (A_3^{1/2} - A_1^{1/2})^2 a / d + 4 (A_2^{1/2} - A_3^{1/2})(A_3^{1/2} - A_1^{1/2})(a + h) / ((d - h)(2 + h/a))]$$

[4]

- A_1 : interaction constant of disperse phase (polystyrene); $7.0 \times 10^{-20} \text{ J}$
 (A_1 was estimated from the Brownian stability factor obtained from the experiment ($\zeta = 10$ with 0.33 M-MgCl_2), and the zeta potential ($\zeta = -20 \text{ mV}$ which is approximated to be equal to the stern potential).
- A_2 : interaction constant of dispersion medium (water); $5.0 \times 10^{-20} \text{ J}$
- A_3 : interaction constant of adsorbed layer (GT or PGUA); $4.6 \times 10^{-20} \text{ J}$
- a : radius of particles; 165 or 245 nm

h : steric layer thickness

d : separation distance; closest separation distance between the surfaces of two spheres ($=2h$ in this approximation)

The force profile for particles having a diameter of 490 nm is shown in Fig. 3.38, 3.39. Figure 3.38 indicates that the potential barrier to the primary maximum is so high that the primary minimum flocculation does not occur. It is most likely that particles flocculate into the secondary minimum resulting from the van der Waals attractive force and the steric repulsive force as shown in Fig. 3.39. Figure 3.39 was drawn combining the van der Waals attraction and the steric repulsion shown in Fig. 3.38. This secondary minimum is located at the point where the steric repulsion begins to take place. The surface force measurements showed that twice the steric layer thickness obtained from PCS corresponds to the separation distance where the steric repulsion begins to appear. Hence, it can be approximated that the particles covered with GT or PGUA flocculate to form doublets at the separation distance, d which is twice the steric layer thickness, h obtained from PCS.

In order to examine this approximation, the stability factors obtained from the turbidimetric technique were compared with those calculated from the secondary minimum flocculation theory as follows.

The depth of the secondary minimum well is equal to the van der Waals force at the separation distance of twice the steric layer thickness obtained from PCS. Using this value for the van der Waals force at the secondary minimum, the secondary minimum stability factor, W_{Smin} can be calculated using Eq. [7] derived below (41).

The flocculation of particles into the secondary minimum can be considered in the same way as the flocculation into the primary minimum. Here, the primary maximum is assumed to be insurmountable and thus the distance of closest approach of two particle centers, R is given by

Fig. 3.38 Force Profile for Particles covered with PGUA (pH 2.0, Ionic Strength = 0.1M-KCl, Particle Diameter = 490 nm)

Fig. 3.39 Secondary Minimum for Particles Covered with PGUA (pH 2.0, Ionic Strength = 0.1M-KCl, Particle Diameter = 490 nm)

$$R=2a+d \quad [5]$$

Because the secondary minimum is relatively shallow and comparable with kT , there will be particles with sufficient energy to escape from the flocculation state. If E is the fraction of total particles arriving at the secondary minimum forming doublets, the fraction of the particles possessing sufficient energy to escape the secondary minimum is $\exp(V_{Smin}/kT)$. Hence,

$$E=1-\exp(V_{Smin}/kT) \quad [6]$$

V_{Smin} : potential energy at the secondary minimum

The secondary minimum stability ratio is therefore given by

$$W_{Smin} = k_{Smolu}/k_{with polymer} \int_R^{\infty} [\exp(V/kT)/r^2]dr / [1 - \exp(V_{Smin}/kT)] \quad [7]$$

k_{Smolu} : flocculation rate constant from the Smoluchowski theory

$k_{with polymer}$: flocculation rate constant in the presence of polymers

V : potential energy at a separation distance of R

The flocculation rate constant from the Smoluchowski theory, k_{Smolu} can be approximated to be equal to the flocculation rate constant in the absence of polymers because an enough amount of salt, 0.33 M was added (rapid flocculation region):

$$k_{Smolu} = k_{without\ polymer}$$

$k_{without\ polymer}$: flocculation rate constant in the absence of polymers

Therefore,

$$W_{Smin} (=W_{calc}) = k_{without\ polymer} / k_{with\ polymer} = W_{exp}$$

W_{exp} : stability factor obtained from the turbidimetric technique

Tables 3.7 and 3.8 list the steric layer thickness obtained from PCS, the van der Waals force (V_A) calculated using Eq. [4], the secondary minimum stability factor (W_{calc}) calculated using Eq. [7], and the secondary minimum stability factor (W_{exp}) obtained from the turbidimetric technique (36, 39). Since the surface force measurements (SFM) indicated that the steric layer thickness for PGUA was underestimated by the PCS, the steric layer thicknesses obtained from PCS were multiplied by a factor of 1.9 (= 35 nm [obtained from SFM] / 18 nm [obtained from PCS]).

Table 3.7 Comparison of W_{exp} obtained from experiments with W_{calc} calculated for GT (particle diameter: 330 nm)

Steric Layer Thickness [nm]	V_A [kT]	W_{calc}	W_{exp}
70	-0.024	50	>100
50	-0.025	40	80
14	-0.074	14	15

Table 3.8 Comparison of W_{exp} obtained from experiments with W_{calc} calculated for PGUA (particle diameter: 490 nm)

Steric Layer Thickness [nm]	V_A [kT]	W_{calc}	W_{exp}
35	-0.042	24	80
19	-0.078	13	60
6	-0.27	4	10

The observed values for W_{calc} were comparable to those for W_{exp} , indicating that the particles flocculate into the secondary minimum. Therefore, the mechanism of the stabilization by the acidic polysaccharides can be explained as follows. The adsorbed polysaccharides give the steric repulsion which prevents the particles from flocculating into the primary minimum. However, the particles slowly flocculate into the secondary minimum in the presence of the polysaccharides. The rate of this secondary minimum flocculation depends on the depth of the secondary minimum. A greater steric layer thickness gives a smaller depth of the secondary minimum because the secondary minimum is located further away from the surface of the particles. Therefore, the greater steric layer thickness gives greater stability. This relation between the steric layer thickness and the stability was observed in the experiments in which the surface charge of the particles, the molecular weight of the polysaccharides, and the solution pH were varied (Table 3.9).

Table 3.9 Relation between the Steric Layer Thickness and the Stability

Parameters		Thickness	Stability
Surface Charge of Particles	negative	large	large
	positive	small	small
Molecular Weight of Polysaccharides	high	large	large
	small	small	small
Solution pH	low	large	large
	high	small	small

3.6.4 Conclusions

- (1) The interaction energy between polysaccharides bearing surfaces is long-ranged and always repulsive. This repulsive interaction is due to a good solvent condition.
- (2) The smaller steric layer thickness compared to $2R_g$ both for gum tragacanth and poly (galacturonic acid) indicates that the polysaccharides are adsorbed with multiple points attached to the surface.
- (3) The hysteresis for compression and decompression both for gum tragacanth and poly (galacturonic acid) indicates that the compressed polysaccharides do not have enough time to move off the surfaces during decompression.
- (4) The thicknesses at which interaction occurs are comparable to the steric layer thickness measured by the photon correlation spectroscopy.
- (5) The greater steric layer thickness gives greater stability because of the smaller depth of the secondary minimum.

CHAPTER 4

PEPTIZATION OF COAL-WATER SLURRIES

4.1 Introduction

The chapter 3 showed that the polystyrene latex particles can be peptized simply by changing the solution pH. In order to see if this peptization occurs for the coal-water slurries, the following experiments were carried out.

4.2 Experimental

4.2.1 Materials

The coal used in these studies was identical for the coal used in the settling tests. Gum tragacanth was purchased from Sigma Chemical Company, and used as received.

4.2.2 Procedures

The 1 wt % of coal-water slurries was used in the experiments. The concentration of GT was 1,000 ppm. The coal-water slurries were first kept in the 20 ml vial for 24 hours at high pH; pH 8. Then the optical density of the supernatant was measured by the spectrophotometer at the wave length of 650 nm after ten times dilution. Next, the pH was lowered to pH 2, and 24 hours later the optical density of the supernatant was again measured. The solution pH was adjusted by adding HCl and NaOH.

4.3 Results and Discussion

Figure 4.1 shows the results for the peptization of coal-water slurries containing GT. The flocculation occurred very rapidly at pH 8, however, after pH was dropped to pH 2, the coal particles stayed stabilized in the solution. Therefore, the peptization was found possible not only for the model systems, but also for the coal-water slurries. The results

from the model studies indicate that this peptization is due to the difference in the conformation of GT adsorbed on the surface.

Fig. 4.1 Flocculation-Peptization-Flocculation of Coal Slurries

CHAPTER 5

SUMMARY

The stabilization of colloidal particles by acidic polysaccharides was found to be due to the steric repulsion. The investigations on the effects of the solution pH, the molecular weight of the polysaccharide, and the surface charge of particles on the stability showed that the steric layer thickness is the factor which determines the stability. This importance of the steric layer thickness for the stability suggested that the greater stability results from the greater steric repulsion. However, without any data on the steric potential, the information about how the particles interact on flocculation is limited. Therefore, the surface force measurements were carried out to obtain directly the force profiles between the surfaces covered with polysaccharides. The results showed that the particles flocculate near the secondary minimum resulting from the van der Waals attractive force and the steric repulsion. In addition, the strong dependency of the stability on the solution pH led one to see if this pH effect can bring about peptization. The peptization was in fact possible not only for the model system, but also for the coal particles.

REFERENCES

- 1) Tadros, T. F., in "Second European Conference on Coal Liquid Mixtures" (The Institute of Chemical Engineers, Ed.). Pergamon Press, New York, 1985.
- 2) Pfizer Inc., Technical Report; "Pfizer Flocon Biopolymers for Industrial Use"
- 3) Bergenstahl, B., Fogler, H. S., and Stenius, P., in "Gums and Stabilisers For the Food Industry 3" (G. O. Phillips, D. J. Wedlock and P. A. Williams, Eds.). p. 285. Elsevier, New York, 1985.
- 4) Sandford, P. A., and Baird, J., in "The Polysaccharides Vol. 2" (G. O. Aspinall Ed.). p. 470. Academic Press, New York, 1983.
- 5) Meer, G., Meer, W. A., and Gerard T., in "Industrial Gums" (R. L. Whisler and J. N. BeMiller, Eds.), 2nd ed., p. 291. Academic Press, New York, 1973.
- 6) Heath, D. and Tadros, T. F., *Colloid & Polymer Sci.*, **261**, 49, 1983.
- 7) Aspinall, G. O., and Baillie, J., *J. Chem. Soc. London*, 1702, 1963.
- 8) Aspinall, G. O., and Baillie, J., *J. Chem. Soc. London*, 1714, 1963.
- 9) Stephen, A. M., in "The Polysaccharides Vol. 2" (G. O. Aspinall Ed.). p. 155, Academic Press, 1983.
- 10) Melik, D. H., and Fogler, H. S., *J. Colloid and Interface Sci.* **92**, (1), 161, 1983.
- 11) Norris, J. R., and Ribbons, D. W., "Methods in Microbiology," Vol. 5B, p. 265. Academic Press, New York, 1971.
- 12) Fler, G. J., and Lyklema, J., in "Adsorption from Solution at the Solid/Liquid Interface" (G. D. Parfitt and C. H. Rochester eds.) p. 214 Academic Press, London, 1983.
- 13) Ohshima, H., and Kondo, T., *J. Colloid Interface Sci.* **116**, 305, 1987.
- 14) Heath, D. and Tadros, T. F., *Colloid & Polymer Sci.* **261**, 49, 1983.
- 15) Lyklema, J., in "Modern Trends of Colloid Science in Chemistry and Biology" (H. F. Eicke, Eds.). Birkhaeuser, Basel, 1985.
- 16) Cosgrove, T., Obey, T. M., and Vincent, B., *J. Colloid Interface Sci.*, **111** (2), 409, 1986.
- 17) May, C. D., and Stainsby, G., in "Gums and Stabilisers for the Food Industry 3" (G. O. Phillips, D. J. Wedlock, and P. A. Williams, Eds.). p. 515, Elsevier, 1986.
- 18) Makino, K., Ohshima, H., and Kondo, T., *J. Colloid Interface Sci.*, **115** (1), 65, 1987.

- 19) Chandar, P., and Somasundaran, P., *Langmuir*, **3**, 298, 1987.
- 20) Byrum, W. R., and Dale, L. B. Jr., *J. Amer. Pharm. Ass.*, **45** (2), 134, 1956.
- 21) Cosgrove, T., Vincent, B., Crowley, T. L., and Cohen Stuart, M. A., in "Polymer Adsorption and Dispersion Stability" (E. D. Goddard and B. Vincent, Eds.). Vol. 240, p. 147, Amer. Chem. Soc., Washington, D. C., 1984.
- 22) Vold, R. D., and Vold, M. J., "Colloid and Interface Chemistry", p. 266, Addison-Wesley, Massachusetts, 1983.
- 23) Yokoyama, A., Srinivasan, K. R., and Fogler, H. S. *J. Colloid Interface Sci.*, in press.
- 24) Cosgrove, T., Obey, T. M., and Vincent, B. *J. Colloid Interface Sci.* **111**, 409, 1986.
- 25) Napper, D. H., "Polymeric Stabilization of Colloidal Dispersions," Academic Press: London, 1983.
- 26) Lichtenbelt, J. W. Th., Pathamamanoharan, C., and Wiersems, P. H. *J. Colloid Interface Sci.*, **49**, 28, 1974.
- 27) Israelachvili, J. N., and Adams, G. E., *J. Chem. Soc. Farad. Trans. I*, **74**, 975, 1978.
- 28) Tadros, Th. F., in "Polymer Adsorption and Dispersion Stability" (E. D. Goddard and B. Vincent Eds.) p. 411 Academic Press, Washington D. C., 1984.
- 29) Klein, J., *JCS Faraday I*, **79**, 99, 1983.
- 30) Derjaguin, B. V., *Kolloid Zh.*, **69**, 155, 1934.
- 31) Derjaguin, B. V., and Landau, L., *Acta Physiochim URSS*, **14**, 633, 1941.
- 32) Verwey, E. J. W., and Overbeek, J. Th. G., "Theory of Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.
- 33) Israelachvili, J. N., and Adams, G. E., *J. Chem. Soc. Farad. Trans.*, **1**, **78**, 975, 1978.
- 34) Vincent, B., in "Solid/Liquid Dispersions" (Th. F. Tadros Ed.) p. 153 Academic Press, London, 1987.
- 35) Afshar-Rad, T., Bailey, A. I., Luckham, P. F., Macnaughtan, W., and Chapman, D., *Colloids and Surfaces*, **31**, 125, 1988.
- 36) Yokoyama, A., Srinivasan, K. R., and Fogler, H. S., to be published in *J. Colloid Interface Sci.*
- 37) Hadziannou, G., Patel, S., Granick, S., and Tirrell, M., *J. Am. Chem. Soc.*, **108**, 2869, 1986.
- 38) de Gennes, P. G., *Macromolecules*, **15**, 492, 1982.

- 39) Yokoyama, A., Srinivasan, K. R., and Fogler H. S., submitted to *Langmuir*.
- 40) Vincent, B., *J. Colloid Interface Sci.*, 42, 270, 1973.
- 41) Reynolds, P. A., and Goodwin, J. W., *Colloids and Surfaces*, 23, 273, 1987.

DOE/PC/80517-T12

IMPROVING THE STABILITY OF COAL SLURRIES

DOE