Dynamics and microstructure of pH-responsive nano-colloidal particles

Tan, Maureen Janet Beng Hoon

2005

Tan, M. J. B. H. (2005). Dynamics and microstructure of pH-responsive nano-colloidal particles. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/6152>

<https://doi.org/10.32657/10356/6152>

Nanyang Technological University

Downloaded on 26 Apr 2023 17:48:39 SGT

Dynamics and Microstructure of pH-Responsive Nano- Colloidal Particles

Maureen Janet Tan Beng Hoon

School of Mechanical & Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2005

ABSTRACT

The characteristics of model pH-responsive nano-colloidal systems consisting of methacrylic acid-ethyl acrylate (MAA-EA) cross-linked with di-allyl phthalate (DAP) and their corresponding interaction potential was manipulated by varying the following: (a) degree of neutralization, α of MAA groups, (b) salt concentration, (c) microgel cross-linked density, and (d) molar ratio of MAA-EA. Neutralization of acid groups increases the osmotic pressure exerted by counter-ions trapped in the polymeric network against the counter-ions in bulk solution, which are responsible for the swelling and viscosity increase. The viscosity exhibits a maximum at ~ 1 wt% DAP and it decreases to a steady value at 4 wt% DAP, which is independent of pH and particle concentrations. Static light scattering results confirmed this optimum density as the critical point where sufficient cross-linked points are present to produce permanent junctions that permit optimal swelling of the nano-colloidal particles.

In addition, the variation of relative swelling with cross-linked densities of the model microgel systems agrees with the theoretical scaling law, $Q \propto (y\alpha N_x)^{3/2}$ for cross-linked densities beyond this optimum point (Q is the swelling ratio, y the acidic MAA content, N_x the cross-linked density, and α is the degree of neutralization). This theoretical scaling law has been successfully expanded to include new data containing microgels with varying [KCl] salt concentrations. Excellent agreement was obtained where all the data fall onto a master curve, which confirmed that the new scaling law, $\frac{N_x}{c_0} (C_{K^+} + C_{Na^+}) Q + Q^{2/3} \propto y N_x \alpha$, is capable of predicting the relative swelling ratio of microgels in different ionic strength solutions (c_0 is the polymer concentration

in the particles at collapsed state, C_{K^+} and C_{Na^+} the concentration of mobile potassium, K^+ and sodium, Na^+ ions respectively in the bulk solution).

These significant findings provided motivation to propose a unified semi-empirical approach for predicting the viscosity of dilute and concentrated hard and soft sphere systems. A variable specific volume, k was introduced to convert the mass concentration to effective volume fraction. With increasing particle concentration, the concentration of free counter-ions in the solution can be large enough to induce an osmotic de-swelling of soft particles, resulting in particle shrinkage. The viscosity data for a wide variety of cross-linked microgel systems as well as core-shell pH-responsive microgels at different neutralization degree showed excellent agreement with the modified Krieger-Dougherty model. The parameters, c' and m for the expression, $k - k_{min} / k_0 - k_{min} = [1 + (c/c')^2]^{-m}$ as a function of α were determined where k_{min} is the limiting specific volume when soft particles are compressed to hard sphere equivalent volume, c' the critical particle concentration at which soft particles start to shrink and m the rate of decrease in k . It was observed that c' decreases with α , while m increases with α . The validity of the new approach was compared to the theoretical model for determining the effective volume fraction, $\phi = \frac{\tilde{Q}}{V_m c_0} \frac{\rho_s}{\rho_p} c$ ($\tilde{Q}$ is the swelling at finite concentration, V_m the molar volume of monomeric units, ρ_s and ρ_p are the specific mass of suspension and polymer respectively) where excellent agreement was observed. This present approach is extremely valuable to scientists and technologists working with soft particles as the flow properties of these interesting systems can be predicted *a priori*.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professors Tam Kam Chiu and Lam Yee Cheong for their continuous guidance, support and encouragement during my experimental studies and interpretation of results. The synthesis of the model polymer systems was carried out by Dow Chemicals, and I would like to acknowledge Dr. Richard Jenkins and Mr. Tan Chee Boon for their contribution to this project. I would like to acknowledge Mr. Dai Sheng and members of the associative polymer group for their help, support and advice, which are vital to the successful progress of this research. I also wish to extend my sincere thanks to all the technical staff and friends in Materials Laboratory for their kind support. Lastly, I would like to thank Nanyang Technological University for providing the financial support to pursue this research project.

On this occasion, I am thankful to my family and beloved husband for their constant encouragement and for giving me their blessing to pursue my studies in Singapore.

LIST OF PUBLICATIONS

Beng H. Tan, Kam C. Tam, Yee C. Lam, Chee B. Tan. Microstructure and Rheology of Stimuli-Responsive Nano-colloidal Systems-effect of cross-linker density. **Advances in Colloid and Interface Science. (In Press)**

Beng H. Tan, Kam C. Tam, Yee C. Lam, Chee B. Tan. Microstructure and Rheology of Stimuli-Responsive Nano-colloidal Systems-effect of ionic strength. **Langmuir**. 2004, *20(26)*, 11380.

Beng H. Tan, Kam C. Tam, Yee C. Lam, Chee B. Tan. Dynamics and Microstructure of Charged Soft Nano-Colloidal Particles. **Polymer**. 2004, *45*, 5515.

Tan, B.H., Tam K.C., Lam Y.C., Tan C.B. A Semi-Empirical Approach for Modeling Charged Soft Microgel Particles. **Journal of Rheology** 2004, *48*, 916.

Beng H. Tan, Kam C. Tam, Yee C. Lam, Chee B. Tan. Dynamics and Microstructure of pH-Responsive Core-shell Particles. **Submitted to Journal of Rheology**.

Beng H. Tan, Kam C. Tam, Yee C. Lam, Chee B. Tan. A Turbidity Study of Stimuli-Responsive Soft Nano-colloidal Systems. **Submitted to Langmuir**.

TABLE OF CONTENTS

ABSTRACT.....	I
ACKNOWLEDGEMENTS	III
LIST OF PUBLICATIONS	IV
TABLE OF CONTENTS	V
LIST OF FIGURES	IX
LIST OF TABLES	XVII
LIST OF SYMBOLS	XVIII
1 INTRODUCTION	1
1.1 OVERVIEW OF pH-RESPONSIVE SOFT PARTICLES	1
1.2 MOTIVATION AND OBJECTIVES FOR THE PROJECT	3
1.3 SURVEY OF THIS THESIS	4
2 LITERATURE REVIEW	8
2.1 SUSPENSION RHEOLOGY	8
2.2 APPROACH TO MODEL HARD SPHERE SUSPENSIONS	10
2.2.1 STEADY SHEAR VISCOSITY	10
2.2.2 SHEAR THINNING	11
2.3 THE RHEOLOGY OF DILUTE POLYMER SOLUTIONS	14
2.3.1 INTRINSIC VISCOSITY AND OVERLAP CONCENTRATION	14
2.4 ELECTRICALLY CHARGED PARTICLES	17
2.4.1 PARTICLE CHARACTERIZATION	17
2.4.2 VISCOSITY	18
2.5 SOFT SPHERE COLLOIDAL PARTICLES	20
2.5.1 CHARACTERISTICS OF MICROGELS	20
2.5.2 SWELLING AND ELASTICITY OF STIMULI-RESPONSIVE MICROGEL	22
2.5.3 APPROACH TO MODEL SOFT PARTICLES	25
2.6 STORAGE AND LOSS MODULUS	30

2.7	STATIC STRUCTURE FACTOR	36
2.7.1	TURBIDIMETRY TO DETERMINE STRUCTURE FACTOR.....	39
2.8	SUMMARY	42
3	MATERIALS AND EXPERIMENTAL TECHNIQUES	43
3.1	SYNTHESIS OF CROSS-LINKED MAA-EA MICROGELS	43
3.2	SYNTHESIS OF CORE-SHELL MICROGELS	45
3.3	PREPARATION OF MICROGEL SAMPLES	48
3.4	NEUTRALIZATION OF MICROGEL SAMPLES.....	50
3.5	EQUIPMENT AND EXPERIMENTAL TECHNIQUES	51
3.5.1	RHEOMETERS AND RHEOLOGICAL MEASUREMENTS	51
3.5.2	ELECTROMOTIVE MEASUREMENTS	53
3.5.3	TURBIDIMETRIC TECHNIQUE	54
3.5.4	LASER LIGHT SCATTERING AND MEASUREMENTS.....	55
4	MICROSTRUCTURE AND RHEOLOGY OF MAA-EA	
	MICROGELS –EFFECT OF CROSS-LINKED DENSITY	60
4.1	SWELLING AND ELASTICITY	60
4.2	STEADY SHEAR VISCOSITY DEPENDENCE ON DEGREE OF NEUTRALIZATION AND MICROGEL CONCENTRATION	64
4.3	OPTIMUM CROSS LINKED DENSITY	66
4.3.1	RHEOLOGICAL ANALYSIS	66
4.3.2	MOLECULAR WEIGHT ANALYSIS	67
4.3.3	THEORETICAL SCALING ANALYSIS	70
4.4	SUMMARY	75
5	MICROSTRUCTURE AND RHEOLOGY OF MAA-EA	
	MICROGELS –EFFECT OF MAA CONTENT.....	76
5.1	SWELLING AND ELASTICITY	76
5.1.1	PARTICLE SIZE CHARACTERIZATION.....	76
5.1.2	THEORETICAL SCALING ANALYSIS	79
5.2	STEADY SHEAR VISCOSITY DEPENDENCE ON DEGREE OF NEUTRALIZATION	81
5.3	DYNAMIC VISCOELASTIC.....	84

5.4	SUMMARY	88
6	MICROSTRUCTURE AND RHEOLOGY OF MAA-EA MICROGELS –EFFECT OF IONIC STRENGTH.....	89
6.1	PARTICLE SIZE CHARACTERIZATION	89
6.2	EFFECT OF IONIC STRENGTH ON MOBILE COUNTER-IONS	91
6.3	THEORETICAL SCALING ANALYSIS.....	94
6.4	STEADY SHEAR VISCOSITY DEPENDENCE ON DEGREE OF NEUTRALIZATION	97
6.5	DYNAMIC VISCOELASTIC.....	99
6.6	SUMMARY	102
7	SEMI-EMPIRICAL APPROACH FOR MODELLING CHARGED SOFT MICROGEL PARTICLES	103
7.1	RHEOLOGICAL BEHAVIOR	104
7.2	MODELLING SOFT PARTICLES USING A CONSTANT SPECIFIC VOLUME, κ	106
7.3	MODELLING SOFT PARTICLES USING A VARIABLE SPECIFIC VOLUME, κ	110
7.4	SUMMARY	121
8	THEORETICAL APPROACH FOR MODELLING CHARGED SOFT MICROGEL PARTICLES	122
8.1	EFFECT OF FREE COUNTER-IONS ON VISCOSITY	122
8.1.1	DETERMINATION OF FRACTION OF FREE COUNTER- IONS USING CALCULATION METHOD	122
8.1.2	DETERMINATION OF FRACTION OF FREE COUNTER- IONS USING EXPERIMENTAL MEASUREMENTS.....	126
8.2	COMPARISON OF SEMI-EMPIRICAL AND THEORETICAL APPROACH.....	130
8.3	SUMMARY	131
9	A TURBIDITY STUDY OF SOFT MICROGEL PARTICLES IN COLLOIDAL SUSPENSIONS	132

9.1	STRUCTURE FACTORS FROM TURBIDIMETRY	132
9.2	STRUCTURE FACTORS AS A FUNCTION OF CROSS-LINKED DENSITY	137
9.3	STRUCTURE FACTORS AS A FUNCTION OF IONIC STRENGTH	139
9.4	SUMMARY	141
10	DYNAMICS AND MICROSTRUCTURE OF CORE-SHELL MICROGEL PARTICLES.....	142
10.1	PARTICLE SIZE CHARACTERIZATION	143
10.1.1	DYNAMIC LIGHT SCATTERING MEASUREMENTS	143
10.1.2	STATIC LIGHT SCATTERING MEASUREMENTS	145
10.2	RHEOLOGICAL BEHAVIOR	147
10.3	SEMI-EMPIRICAL APPROACH TO MODEL CORE-SHELL PARTICLES.....	149
10.4	THEORETICAL APPROACH TO MODEL CORE-SHELL PARTICLES.....	153
10.5	STRUCTURE FACTORS FROM TURBIDITY	155
10.5.1	STRUCTURE FACTORS AS A FUNCTION OF NEUTRALIZATION DEGREE AND IONIC STRENGTH	156
10.6	SUMMARY	158
11	CONCLUSIONS.....	159
12	RECOMMENDATIONS FOR FUTURE WORK	162
	REFERENCES.....	164
	APPENDIX A	172
	APPENDIX B	174

LIST OF FIGURES

Figure 2.1	The shear rate dependence of the apparent relative viscosity, η_{rA} = suspension viscosity / plastisizer viscosity, of flocculation stable plastisols at dilute through intermediate volume fractions. η_r = suspension viscosity / supernatant viscosity after centrifugation (dashed line) [Bossis and Brady, 1989].....	12
Figure 2.2	Relative viscosity versus dimensionless shear rate for sterically stabilized monodisperse suspensions of PVC plastisols at $\phi=0.20$. Open symbols (PVC-A, $D_d=293$ nm); half-filled (PVC-B, $D_d=619$ nm); solid symbols (PVPVC-C, $D_d=1154$ nm) [Willey et al., 1978].....	13
Figure 2.3	Effect of added electrolyte on the relative viscosity of polystyrene latex suspension with diameter of $0.11 \mu\text{m}$ at $\phi = 0.40$. $\bigcirc$: Deionized; $\square$: 1.876×10^{-4} M HCl; $\blacksquare$: 1.876×10^{-3} M; $\blacktriangle$: 9.378×10^{-2} M; $\bullet$: 1.876×10^{-2} M [Russel, 1980].....	19
Figure 2.4	Variation of the $[\eta]$ of microgels formed by emulsion polymerization. The experimental data points were taken from the following sources.	21
Figure 2.5	(a) variation of the swelling ratio at maximum swelling versus the cross-linked density. (b) variation of the swelling ratio with the neutralization degree for $N_X=140$ ($\bullet$), $N_X=70$ ($\blacklozenge$), $N_X=28$ ($\blacktriangle$) [Cloitre et al., 2003].	23
Figure 2.6	η_0/η_s of PNIPAM particles at different temperatures versus. polymer concentration in weight percent. The lines display fits according to Equation (2.21) [Senff et al., 2000].	26
Figure 2.7	Illustration of frequency-dependent storage and loss moduli G' and G'' for a typical “liquid-like” and “solid-like” materials.	31
Figure 2.8	Yield stress for 2wt% cross-linked PNIPAM at microgel concentration of 6.8wt%: shear rate (filled symbols) and strain (open symbols) as a function of the shear stress for different temperatures [Senff et al., 1999].	32
Figure 2.9	Elastic modulus, G' (filled symbols) and loss modulus, G'' (open symbols) versus frequency for 4wt% cross-linked PNIPAM at microgel concentration of 7.15 wt% and temperatures, $\blacksquare$: 10°C ; $\blacktriangle$: 20°C and $\blacklozenge$: 30°C [Senff et al., 1999].	33

Figure 2.10	Double-logarithmic plot of the plateau modulus against the effective volume fraction for 4wt% cross-linked PNIPAM with a power-law fit [Senff et al., 1999].	33
Figure 3.1	Chemical structure of model (a) pH-responsive cross-linked MAA-EA microgel and (b) MMA core.	46
Figure 3.2	Schematic representation of Brookhaven laser light scattering system [Brookhaven Instrument Corporation, 1993].	57
Figure 4.1	Schematic representation of microgel particles in the swollen state, cross-linked at different density; (a) low cross-linked density (HASE-20-80-1) and (b) high cross-linked density (HASE-20-80-4). The full dots between chain segments represent the cross-linker. The counterions from the base (NaOH) used to neutralized the microgels are represented by the symbol Na^+ and the symbol $\ominus$ represents the neutralized carboxylic groups, COO^- . The outer shell represents the region where electro-neutrality is not satisfied locally.	61
Figure 4.2	(a) Dependence of hydrodynamic radius, R_h on neutralization degree, α for microgels with 20 mole percent MAA cross-linked at different DAP density (wt% DAP) in salt free solutions; (b) Low shear relative viscosity, η_r as a function of neutralization degree, α of salt free suspension at 5wt% microgel concentration with 20 mole percent MAA cross-linked at different DAP density (wt% DAP).	62
Figure 4.3	Relative viscosity, η_r versus shear rate of salt free microgel suspension at 5wt% polymer concentration with 20 mole percent MAA at four different degree of neutralization, α ($\circ$:0 ; $\diamond$:0.5 ; $\square$:0.8 ; $\triangle$:1.0) and four different cross-linked density (wt% DAP): (a) 0.5 wt%; (b) 1.0 wt%; (c) 2.0 wt%; and (d) 4.0 wt%. The solid lines represents fittings according to Equation (4.1).	65
Figure 4.4	Relative viscosity, η_r as a function of cross-linked density (wt% DAP) of microgel with 20 mole percent MAA at; (a) polymer concentration of 5 wt% with different neutralization degree, α and; (b) different polymer concentration, c (wt%) of the fully neutralized microgel ($\alpha=1$).	66
Figure 4.5	Zimm plot of HASE-20-80-2 at (a) $\alpha=0$ and (b) $\alpha=1$ in aqueous solution at room temperature where the polymer concentration range was from 0.001 to 0.01 mg/ml.	67
Figure 4.6	Results from static light scattering illustrating the dependence of (a) molecular weight, M_w and (b) second virial coefficient, A_2 on cross-linked density (wt% DAP) of microgel with 20 mole percent MAA both at the unneutralized ($\alpha=0$) and fully neutralized state ($\alpha=1$).	68

- Figure 4.7** Results from static light scattering illustrating the dependence of (a) molecular weight, M_w and (b) second virial coefficient, A_2 , on neutralization degree, α of HASE-20-80-0.5 and HASE-20-80-2. 69
- Figure 4.8** (a) Variations of the maximum swelling ratio, Q_m at $\alpha=1$ as a function of cross-linked density, $N_x^{3/2}$. Solid line represents the region where Equation (2.19) is valid; (b) Variations of the normalized swelling ratio Q/Q_m as a function of α , for microgel with 20 mole percent MAA at different cross-linked densities (wt% DAP) (● :0.5 ; □ : 0.75 ; ▲ :1.0 ; ○ :1.5 ; ■ : 2.0 ; △ :3.0 ; ◆ :4.0). The master curve is represented by the solid line..... 71
- Figure 4.9** Variations of the swelling ratio, Q as a function of $(\alpha N_x)^{3/2}$ for microgels with varying cross-linked densities, N_x and neutralization degree, α . The solid line and the dotted line represents the master curve for the data at $\alpha \geq 0.4$ and $\alpha \leq 0.3$ respectively..... 72
- Figure 4.10** Illustration of the conformational transition for the cross-linked microgel particle with 20 mole percent MAA as function of cross-linked density (wt% DAP). The filled circle represents M_w and the open circle represents the low shear relative viscosity at 5 wt% polymer concentration..... 74
- Figure 5.1** (a) Dependence of hydrodynamic radius, R_h on neutralization degree, α for microgels cross-linked with 4 wt% DAP at different MAA/EA molar ratio in salt free solutions; (b) Low shear relative viscosity, η_r as a function of neutralization degree, α of salt free suspension at 5wt% microgel concentration with different MAA/EA molar ratio. 77
- Figure 5.2** Variations of the swelling ratio, Q as a function of $(y \alpha N_x)^{3/2}$ for microgels with varying cross-linked densities, N_x , molar fraction of MAA units, y and neutralization degree, α . The solid line and the dotted line (see inset graph) represents the fitted line when the data was curve fitted at $\alpha \geq 0.4$ and $\alpha \leq 0.3$ respectively. The linear equations of the fitted lines are shown in the figure..... 80
- Figure 5.3** Shear viscosity, η versus shear rate at five different degree of neutralization, α (○ :0 ; ▲ :0.2 ; ◇ :0.5 ; □ :0.8 ; △ :1.0) of HASE cross-linked with 4 wt% DAP with different MAA/EA molar ratio : (a) 20/80; (b) 30/70; (c) 40/60; and (d) 50/50. 81
- Figure 5.4** (a) Shear rate for the onset of shear-thinning and (b) Power law index, n for the shear thinning region as a function of neutralization degree, α , for microgels cross-linked with 4 wt% DAP at different MAA/EA molar ratio; (◆) 20/80; (○) 30/70; (■) 40/60; and (△) 50/50. 82

Figure 5.5	Storage and loss modulus, G' and G'' as a function of frequency, ω of HASE-40-60-4 microgel at different conditions; (a) varying microgel concentrations, c (wt%) and (b) varying neutralization degree, α	85
Figure 5.6	Plateau modulus, G_p as a function of effective volume fraction, ϕ_{eff} at different neutralization degree, α . The solid line represents the master-curve and the dotted line is to illustrate the two different regions of viscoelasticity.....	87
Figure 6.1	Results from dynamic light scattering illustrating the dependence of R_h on α for (a) HASE-20-80-2 at different salt concentrations, $[KCl]$ and (b) HASE-20-80 with different cross-linked density at salt concentration of 100 mM KCl.	90
Figure 6.2	Concentration of mobile counter-ions (a) potassium, C_{K^+} and (b) sodium, C_{Na^+} , calculated using the Nernst equation, Equation (3.2) and (3.3) for HASE-20-80-2 at varying α and four different salt concentrations, $[KCl]$	92
Figure 6.3	A pictorial representation of the effect of salt (K^+) on the counter-ions (Na^+) inside the microgels and in the bulk solution at different salt concentration regimes; (a) low salt; and (b) high salt environment.	93
Figure 6.4	Variations of $\frac{N_x}{c_0}(C_{K^+} + C_{Na^+})Q + Q^{2/3}$ as a function of $yN_x\alpha$ for (a) HASE-20-80-2 at different salt concentrations, $[KCl]$ and (b) HASE-20-80 with different cross-linked density at salt concentration of 100mM KCl. The master curve is represented by the solid line.	96
Figure 6.5	(a) Shear viscosity, η versus shear rate of four different salt concentrations (mM KCl) of HASE-20-80-2 at 5 wt% polymer concentration and $\alpha=1$. (b) Low-shear relative viscosity, $\eta_r(\eta_0/\eta_s)$ versus the degree of neutralization, α for four different salt concentrations (mM KCl) of HASE-20-80-2 at 5 wt% polymer concentration.	98
Figure 6.6	Storage modulus, G' and loss modulus, G'' as a function of angular frequency, ω for four different salt concentrations (mM KCl) of HASE-60-40-4 at 5 wt% polymer concentration and $\alpha=1$	99
Figure 6.7	Plateau modulus, G_p as a function of effective volume fraction, ϕ_{eff} for four different salt concentrations, mM KCl of HASE-60-40-4 at 5 wt% polymer concentration and $\alpha=1$. The solid line represents the master-curve and the dotted line is to illustrate the two different regions of viscoelasticity.....	100

Figure 7.1	Relative viscosity versus shear rate of cross-linked MAA-EA microgel at 5wt% polymer concentration and four different conditions; (a) varying degree of neutralization (α); (b) varying salt concentrations (mM KCl); (c) varying microgel cross-linked density (wt% DAP); and (d) varying molar ratio of MAA groups (% MAA). The solid lines denote mathematical fittings according to Equation (4.1).....	105
Figure 7.2	Relative viscosity versus polymer concentration, c of HASE-20-80-2 at six different neutralization degrees. Solid lines represent fits according to Equation (2.21).....	106
Figure 7.3	Relative viscosity versus ϕ_{eff} of microgel system (HASE-20-80-2). (a) Dilute solution region at four different salt concentrations, [KCl] ($\triangle$:0.1 mM; $\square$:1 mM; $\circ$:10 mM; $\diamond$:100 mM) and three different α s ; $\alpha=0.5$ (grey), $\alpha=0.8$ (open) and $\alpha=1.0$ (black). Dark solid line denotes Batchelor's equation (Equation (2.20)) (b) Dilute to concentrated region at salt concentration of 0.1 mM KCl for three α s,.....	109
Figure 7.4	A pictorial representation of the changes in the specific volume k at three different concentration regimes; (a) dilute; (b) semi-dilute; and (c) concentrated region.	110
Figure 7.5	Specific volume, k as a function of concentration of cross-linked MAA-EA microgel at four different conditions; (a) varying degree of neutralization (α); (b) varying salt concentrations (mM KCl); (c) varying microgel cross-linked density (wt% DAP); and (d) varying molar ratio of MAA groups (% MAA). The solid lines denote mathematical fittings according to Equation (7.1).....	112
Figure 7.6	(a) c_0 (filled symbols) and (b) m (open symbols) as a function of degree of neutralization, α of HASE-20-80-2 microgel system at four different salt concentrations, [KCl]; ($\triangle$:0.1 mM; $\square$:1 mM; $\circ$:10 mM; $\diamond$:100 mM).	114
Figure 7.7	$\partial k / \partial c$ as a function of concentration of cross-linked MAA-EA microgel at four different conditions; (a) varying degree of neutralization (α); (b) varying salt concentrations; (c) varying microgel cross-linked density; and (d) varying molar ratio of MAA groups. The solid lines are to guide the eye, which shows the increasing trend of m and the reducing trend of c_0 as the conditions vary.....	116
Figure 7.8	Relative low shear viscosity versus effective volume fraction of cross-linked MAA-EA microgel systems at four different conditions; (a) neutralization degree (α) of MAA groups; (b) salt concentration; (c) microgel cross-linked density; and (d) molar ratio of MAA groups. The solid line and the dotted line denote the hard sphere behavior according to Equation (2.20) and Equation (2.3) respectively.	118

- Figure 8.1** Relative low shear viscosity versus effective volume fraction determined from Equation (2.27) where Γ was calculated from Equation (2.23) and (2.24) for cross-linked MAA-EA microgel systems with varying cross-linked densities; (a) HASE-20-80-1, (b) HASE-20-80-2, (c) HASE-20-80-3 and (d) HASE-20-80-4 and varying MAA content; (e) HASE-40-60-4 and (f) HASE-50-50-4 at three different α s (Δ : $\alpha=0.5$; $\square$: $\alpha=0.8$; $\circ$: $\alpha=1.0$. The solid line denotes the hard sphere behavior according to Equation (2.3)..... 125
- Figure 8.2** Comparison of values of Γ measured using Na^+ ISE (filled symbols) with the values calculated from the Debye length (Equation (2.23) and (2.24)) (open symbols) at three different α s (Δ : $\alpha=0.5$; $\square$: $\alpha=0.8$; $\circ$: $\alpha=1.0$) for microgel systems with low cross-linked densities; (a) HASE-20-80-1 and (b) HASE-20-80-2 and high MAA content; (c) HASE-40-60-4 and (d) HASE-50-50-4. 127
- Figure 8.3** Relative low shear viscosity versus effective volume fraction calculated from Equation (2.27) for cross-linked MAA-EA microgel systems with varying cross-linked densities; (a) HASE-20-80-1, (b) HASE-20-80-2, (c) HASE-20-80-3 and (d) HASE-20-80-4 and varying MAA content; (e) HASE-40-60-4 and (f) HASE-50-50-4 at three different α s (Δ : $\alpha=0.5$; $\square$: $\alpha=0.8$; $\circ$: $\alpha=1.0$). The open symbols represent ϕ_{eff} determined when Γ was calculated from Equation (2.23) and (2.24) whereas the filled symbols represents ϕ_{eff} calculated from the values of Γ measured using Na^+ ISE. The solid line denotes the hard sphere behavior according to Equation (2.3)..... 129
- Figure 8.4** Comparison of values of ϕ_{eff} determined using the semi-empirical approach (Equation (7.3)) (open symbols) with the theoretical approach (Equation (2.27)) where values of Γ was measured using Na^+ ISE (filled symbols) of microgel systems; (a) HASE-20-80-1 and (b) HASE-50-50-4 at two different α s (Δ : $\alpha=0.5$; $\circ$: $\alpha=1.0$). 131
- Figure 9.1** Turbidity measurements obtained from UV-visible spectroscopy for six different microgel concentrations of HASE-20-80-2 in salt free solution and $\alpha=1$. (a) Transmittance, I_t/I_0 as a function of wavelength, λ , and (b) turbidity, τ as a function of wavelength, λ 133
- Figure 9.2** Specific turbidity, τ/c as a function of microgel concentration, c at fixed wavelength, λ of HASE-20-80-2 in salt free solution and $\alpha=1$. The solid lines are the linear curve fits to the data to extract the intercept, $(\tau/c)_{c=0}$ 134
- Figure 9.3** Integrated structure factor, $Z(\lambda^2, c)$ as a function of $1/\lambda^2$ at different microgel concentration, c of HASE-20-80-2 in salt free solution and $\alpha=1$. The solid lines are the linear curve fits to the data to extract the

intercept, which equals the structure factor of the colloidal particles in the zero angle limit ($S_{cc}(0)$).	136
Figure 9.4 Osmotic compressibility, $S_{cc}(0)$ of fully neutralized ($\alpha=1$) microgels with 20 mole% MAA in salt free solutions at three different cross-linked densities as a function of (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{eff} = k c$. The solid lines are to guide the eye, which shows the reducing trend of $S_{cc}(0)$ as the cross-linked densities vary.	138
Figure 9.5 Osmotic compressibility, $S_{cc}(0)$ of HASE-20-80-2 at $\alpha=1$ and three different salt concentrations, mM KCl as a function of (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{eff} = k c$. The solid lines are to guide the eye, which shows the reducing trend of $S_{cc}(0)$ as the salt concentrations vary.....	140
Figure 10.1 Schematic representation of the core-shell pH-responsive microgel particles at different state, (a) unneutralized ($\alpha=0$) and (b) fully neutralized ($\alpha=1$). The black core represents the PMMA particle and the full dots between chain segments in the shell represent the cross-linker. The counter-ions from the base (NaOH) used to neutralized the microgels are represented by the symbol Na^+ and the symbol $\ominus$ represents the neutralized carboxylic groups, COO^- . The outer shell represents the region where electro-neutrality is not satisfied locally.	142
Figure 10.2 (a) Dependence of shell thickness, R_h-R_c on neutralization degree, α for core-shell microgels with different mole percent MAA, (a) CS-20-80-2 and (b) CS-50-50-1, in different salt concentrations (mM KCl); (Δ : 0.1 mM; $\circ$: 10 mM; $\square$: 100 mM).	144
Figure 10.3 The ratio of R_g/R_h as a function of neutralization degree, α obtained from static and dynamic light scattering for core-shell microgels with different mole percent MAA, (a) CS-20-80-2 and (b) CS-50-50-1, in different salt concentrations (mM KCl); (Δ : 0.1 mM; $\circ$: 10 mM; $\square$: 100 mM).	146
Figure 10.4 Viscosity versus shear rate of model core-shell microgels at four different conditions; (a) varying microgel concentration, c (wt%) of CS-50-50-1; (b) varying neutralization degree (α) of MAA groups of CS-50-50-1; (c) varying salt concentrations (mM KCl) of CS-50-50-1 and (d) varying molar ratio of MAA groups (% MAA). The solid lines denote mathematical fittings according to Equation (4.1).	148
Figure 10.5 Specific volume, k as a function of concentration of particles for three different core-shell microgel systems namely; (a) CS-50-50-1 at varying degree of neutralization (α) of MAA groups; (b) CS-50-50-1 at varying salt concentrations (mM KCl); and (c) varying molar ratio of MAA groups (% MAA). The solid lines denote mathematical fittings according to Equation (7.1).....	150

- Figure 10.6** (a) c_0 and (b) m , as a function of α for CS-20-80-2 (open symbols) and CS-50-50-1 (filled symbols) at three different salt concentrations, (mM KCl). 151
- Figure 10.7** Relative viscosity versus ϕ_{eff} of core-shell systems; (a) CS-20-80-2 and (b) CS-50-50-1 at three different α s ; (Δ : $\alpha=0$; $\circ$: $\alpha=0.5$; $\square$: $\alpha=1.0$) and three different salt concentrations, [KCl] ; no salt (open), 10 mM (grey) and 100 mM (black). Solid line denotes the K-D model (Equation (2.3)). 152
- Figure 10.8** Relative low shear viscosity versus effective volume fraction, ϕ_{eff} of core shell particles with varying MAA content in salt free solutions; (a) CS-20-80-2 and (b) CS-50-50-1 at two different α s (Δ : $\alpha=0.5$; $\circ$: $\alpha=1.0$). ϕ_{eff} was calculated from Equation (2.27) where Γ was measured using Na^+ ISE and the solid line denotes the hard sphere behavior according to Equation (2.3). 153
- Figure 10.9** Comparison of values of ϕ_{eff} determined using the semi-empirical approach (Equation (7.3)) (open symbols) with the theoretical approach (Equation (2.27)) where values of Γ was measured using Na^+ ISE (filled symbols) of core-shell systems in salt free solutions; (a) CS-20-80-2 and (b) CS-50-50-1 at two different α s (Δ : $\alpha=0.5$; $\circ$: $\alpha=1.0$). 154
- Figure 10.10** (a) Specific turbidity, τ/c as a function of microgel concentration, c at fixed wavelength, λ and (b) integrated structure factor, $Z(\lambda^2, c)$ as a function of $1/\lambda^2$ at different microgel concentration, c of CS-50-50-1 in salt free solution and $\alpha = 1$. The solid lines are the linear curve fits to the data to extract the intercept. 155
- Figure 10.11** Osmotic compressibility, $S_{\text{cc}}(0)$ of core-shell microgels, CS-50-50-1 in salt free solutions at varying degree of neutralization, α as a function of, (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{\text{eff}} = k c$ The solid lines are to guide the eye, which shows the reducing trend of $S_{\text{cc}}(0)$ as α vary. 156
- Figure 10.12** Osmotic compressibility, $S_{\text{cc}}(0)$ of fully neutralized ($\alpha=1$) core-shell microgels, CS-50-50-1 at varying salt concentrations (mM KCl) as a function of, (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{\text{eff}} = k c$ The solid lines are to guide the eye, which shows the reducing trend of $S_{\text{cc}}(0)$ as [KCl] vary. 157

LIST OF TABLES

Table 3.1	Characteristic of model pH-responsive (a) cross-linked MAA-EA microgel series and (b) core-shell microgel series.	47
Table 7.1	Results for dynamic light scattering and viscometric measurements of dilute HASE-20-80-2 at different α and salt concentrations.	107
Table 7.3	Summary of the fitted parameters k_0 , c_0 , and m for all the four systems discussed; neutralization degree (α) of MAA groups, salt concentration, microgel cross-linked density, and molar ratio of MAA groups.	120

LIST OF SYMBOLS

α :	Degree of neutralization
a :	Radius of particle
δ :	Mean spacing between particles
R_h :	Hydrodynamic radius (nm)
R_g :	Radius of gyration (nm)
η :	Shear viscosity
η_s :	Solvent viscosity
η_0 :	Zero shear viscosity
η_∞ :	High shear viscosity
η_r :	Relative viscosity
η_{rA} :	Apparent relative viscosity
$\frac{\eta_0}{\eta_s}$:	Relative zero shear viscosity
$\frac{\eta_\infty}{\eta_s}$:	Relative infinite shear viscosity
$\dot{\gamma}$:	Shear rate
$\dot{\gamma}_r$:	Dimensionless shear rate
$\dot{\gamma}_s$:	Shear rate at the onset of shear thinning
γ :	Shear strain
τ :	Shear stress
Pe :	Peclet number

t_D :	Time taken for particle to diffuse a distance equal to its radius
$[\eta]$:	Intrinsic viscosity
K_H :	Huggins coefficient
G' :	Storage modulus
G'' :	Loss modulus
G_p :	Plateau modulus
ω :	Frequency of oscillation in radians per second
$\tau(t)$:	Shear stress
γ_0 :	Strain amplitude
$g(r)$:	Radial distribution function
r :	Center-center separation between particles
$\psi(r)$:	Pair interaction potential.
ϕ_{eff} :	Effective Volume fraction
d_{eff} :	Effective particle diameter
ϕ_m :	Maximum packing fraction
k :	Specific volume, ml/g
k_{min} :	Limiting specific volume when soft particles are compressed to hard sphere equivalent volume
c :	Mass concentration of the dispersion in g/ml
c^* :	Critical particle concentration in g/ml at which particles start to shrink
m :	Rate of decrease in k as a function of c
$\bar{M}_w$:	Weight-average molecular weight of polymer cluster
A_2 :	Second virial coefficient
(dn/dc) :	Refractive index increment of the polymer solution

Π_{in} :	Osmotic pressure of the mobile ions inside the microgels
Π_{out} :	Osmotic pressure of the mobile ions in bulk solution
Π_{el} :	Elastic pressure of the polymeric network
C_{in} :	Concentration of counter-ions inside microgel
C_{out} :	Concentration of counter-ions outside microgel
C_{K^+} :	Concentration of mobile potassium, K^+ ions in bulk solution
C_{Na^+} :	Concentration of mobile sodium, Na^+ ions in bulk solution
Q :	Swelling ratio at infinite dilution
$\tilde{Q}$:	Swelling ratio at finite concentration
N_x :	Cross-linked density, N_x
y :	Molar fraction of methacrylic acidic groups
x :	Molar fraction ethyl acrylate groups
c_0 :	Polymer concentration inside the particles at collapsed state
C_{MAA} :	Concentration of methacrylic acidic groups
V_m :	Molar volume of monomeric units
ρ_s :	Specific mass of suspension in g/ml
ρ_p :	Specific mass of polymer in g/ml
κ_{in}^{-1} :	Debye length
Γ :	Fraction of counter-ions in the solution
l_B :	Bjerrum length
N_A :	Avogadro number
$P(Q)$:	Form factor
$S(Q)$:	Static structure factor
κ_T :	Osmotic compressibility

I_0 :	Incident intensity of the light
I_t :	Transmitted intensity of the light
l :	Length of the optical path
τ :	Turbidity
$R(q)$:	Rayleigh ratio for unpolarized light
q :	Magnitude of the scattering vector
θ :	Scattering angle
n_0 :	Refractive index of the medium
n_p :	Refractive index of the immersed particles
λ :	Wavelength
d :	Diameter of the particles
m :	Relative refractive index
$Q(\lambda^2)$:	Integrated form factor
$Z(\lambda^2, c)$:	Integrated structure factor

1 INTRODUCTION

1.1 OVERVIEW OF pH-RESPONSIVE SOFT PARTICLES

The colloidal phenomenon of soft particles is becoming an important field of research due to the growing interest in a variety of important systems found in biological science, such as vesicles, bilayers, membranes, and living cells. In order to understand the behavior of these complex systems, simpler model systems were developed, where the fundamental science is better described. In addition, such systems provide a platform to understand the physical forces that control their behavior.

Synthetic mono-disperse stimuli-responsive colloids in the nano to micron size range are increasingly becoming important model systems for the study of a variety of phenomena observed in soft condensed matter physics, such as glass transitions and crystal nucleation. They are interesting systems, whose rheological profiles can be modified by external stimuli, such as pH, temperature, ionic strength, electric field, light intensity and an introduction of specific molecules.

In recent years, modern experimental and theoretical methodologies have provided new insights into the rheological behavior of soft pH-responsive colloids containing carboxylic acid latices. During the alkalization of these aqueous dispersions of carboxylic acid-containing latices, the viscosity and shear thinning increase dramatically, making this class of materials useful for rheology control applications [Shay, 1989; Quadrat et al., 1990]. Besides their technical applications (e.g. surface coatings, rheological control and stabilizing agents) pH-responsive colloids are

promising candidates for the development of biochemical and biomedical applications and controlled drug delivery systems.

Previous studies on the swelling of carboxylic acid-containing latices have focused mainly on uncross-linked particles that may have substantial dissolution, in addition to particle swelling, upon neutralization [Muroi et al., 1967; Verbrugge, 1970]. The resulting complex mixture of dissolved linear polymer chains and compositional heterogeneous swollen particles does not permit detailed fundamental understanding of the dispersion structure and its influence on the rheology. As a first step towards developing a generalized approach to model soft pH-responsive particles, it is important to determine the swelling behavior and rheological properties of mono-disperse, internally cross-linked, alkali swellable microgel particles. This system does not undergo substantial dissolution upon neutralization but possesses a better-defined structure, which will allow detailed fundamental study of its microstructure and bulk rheological properties.

Model pH-responsive microgels consisting of methacrylic acid-ethyl acrylate (MAA-EA) cross-linked with di-allyl phthalate (DAP) as well as core-shell pH-responsive microgels consisting of PMMA particles grafted with a soft shell, were synthesized via the emulsion polymerization technique. The polymers are insoluble latices at low pH. By increasing the pH, the ionization of acid groups is enhanced, which increases the solubility and electrostatic repulsion between polymer chains, yielding interesting changes in the particle interaction potential. Using pH-responsive colloids as model systems has the advantage of influencing the particle diameter through pH changes

and with it the rheological properties, which are generally a function of the volume fraction.

1.2 MOTIVATION AND OBJECTIVES FOR THE PROJECT

The objective of the present research is to develop a unified semi-empirical approach for predicting the viscosity of dilute and concentrated hard and soft sphere systems. This is achieved by performing quantitative studies to investigate the swelling behavior (microscopic) and rheological (macroscopic) properties of the pH responsive, internally cross-linked MAA-EA microgel particles and core-shell particles as a function of neutralization degree, ionic strength, and cross-linked density. It is hoped that such studies will provide a molecular-level understanding on the swelling mechanism of the microgels at varying degree of neutralization. In addition, new insights into the effects of varying the microstructure of these microgels on the bulk rheological behavior, for example the viscosity and shear-thinning characteristic of the microgels can be elucidated. Two different model pH-responsive microgel systems were studied; i.e.

1. microgels containing different MAA/EA molar ratio and chemically cross-linked to different cross-linked density using a cross-linker.
2. core-shell pH-responsive microgels consisting of PMMA core, grafted with a soft shell containing different MAA/EA molar ratio and chemically cross-linked to different cross-linked density using a cross-linker.

These experimental studies were carried out using light scattering techniques (both static and dynamic), electromotive (EMF) measurements, turbidimetry and

rheological techniques. Light scattering was used to measure the hydrodynamic radius, R_h , radius of gyration, R_g , and average particle molecular weight, M_w which provides insights into the neutralization and microstructure behavior of the cross-linked MAA-EA microgels as well as the core-shell microgels.

The osmotic-deswelling properties of microgel particles can be accurately studied by electromotive (EMF) measurements where the concentration of free sodium (Na^+) and potassium (K^+) ions, which act as counter-ions were determined using Na^+ and K^+ ion selective electrodes (ISE). On the other hand, experiments conducted using rheometers provide information on the macroscopic property; i.e. the particle interaction potential as a function of degree of neutralization and microgel concentration. The low-shear and high-shear viscosity as well as the severity of shear thinning can be determined by analyzing the viscosity curves as a function of shear rates and shear stress. In addition, turbidimetric methods provide a means to obtain information on the structural factors of the microgel suspensions, which can be used to corroborate the particle interaction potential determined from the rheometry technique.

1.3 SURVEY OF THIS THESIS

Chapter 2 provides an overview of previous works to model hard and soft colloidal systems. In addition, the later part of Chapter 2 summarizes the fundamental knowledge of rheological and flow behavior of colloidal particles as well as microgel systems. Description of the chemical structure, synthesis and characteristics of the polymers and other chemical agents used and experimental procedures are provided in

Chapter 3. Chapter 4 examines the effect of varying cross-linked densities on the rheological behavior of the pH-responsive MAA-EA microgels at fixed MAA/EA molar ratio. The existence of an optimum cross-linked density for a particular MAA/EA molar ratio is also discussed in this chapter. Chapter 5 presents a detailed rheological study on the influence of MAA/EA molar ratio of the microgels at fixed cross-linked density. Also, the later part of Chapter 5 reports the dynamic viscoelastic properties of cross-linked microgels with high MAA content. The effect of varying salt environment on the swelling and rheological behavior of cross-linked MAA-EA microgels are discussed in Chapter 6. In Chapter 7, a unified semi-empirical approach was proposed to predict the viscosity of dilute and concentrated hard and soft sphere colloidal systems. The validity of this new approach is then compared against a theoretical approach and this summary is given in Chapter 8. In addition, Chapter 9 presents the turbidimetric method as a means to obtain information on the structure factors of the microgel suspensions, which can be used to corroborate the particle interaction potential as obtained from the rheometry technique. The new semi-empirical approach is expanded to core-shell pH-responsive microgels consisting of hard PMMA particles grafted with a soft layer of cross-linked MAA-EA copolymers and the validity and limitations are examined in Chapter 10. Finally, Chapter 11 concludes the report and Chapter 12 recommends experiments for future studies.

2 LITERATURE REVIEW

As a first step towards developing a generalized approach to model soft condensed matter, it is vital to understand the fundamental science governing the rheological behavior of hard sphere suspensions, including the mathematical modeling of their behavior, which has been well-established since the early 1900s. The early part of this chapter provides an overview of previous studies on the modeling of dilute and concentrated hard sphere systems.

2.1 SUSPENSION RHEOLOGY

A suspension, or perhaps more broadly a dispersion, consists of discrete particles randomly distributed in a fluid medium. Suspensions of small particles of less than 1 micron are often called “colloids,” a term which describes a substance that could not diffuse through a membrane and is dictated by Brownian dynamics. The performance properties of these fluids depend on their components and the control of these fluid properties evidently depends on an understanding of colloidal rheology.

Literally, rheology means the study of flow and deformation of matter under the influence of an imposed stress. The response of the material to deformation can be divided into two types: flow and elasticity. Flow is irreversible deformation; i.e., when stress is removed, the material does not revert to its original configuration. Elasticity, on the other hand is the reversible response to deformation where the

materials do not dissipate all the deformational energy. The best way to describe real materials is to consider them as viscoelastic as they exhibit both viscous and elastic properties.

The simplest suspensions are composed of hard spheres where the only interaction between particles is rigid repulsions that occur when particles come into close contact. Rheology can be a powerful tool for identifying certain structural features and the interaction forces in colloidal suspensions. [Riddle, 1977; Goddard, 1978].

2.2 APPROACH TO MODEL HARD SPHERE SUSPENSIONS

2.2.1 STEADY SHEAR VISCOSITY

The generalized approach to model hard sphere particles has a long history, dating back to the early 1900s. Einstein first proposed a simple relationship to describe non-interacting hard sphere particles in dilute solutions. This famous relationship (Equation (2.1)), known universally as the Einstein equation described the concentration effect of relative viscosity of dilute suspension systems [Einstein, 1906, 1911],

$$\frac{\eta_0}{\eta_s} = 1 + 2.5\phi \quad (2.1)$$

where η_0 is the viscosity of the suspension, η_s the viscosity of the medium (or solvent) and ϕ is the volume fraction of the suspension. The Einstein relation is obeyed; at least at high shear rates and low concentrations, $\phi < 0.03$. However, for larger ϕ , particle interactions become significant and the Einstein relation breaks down. The next major contribution is attributed to Batchelor in 1977, where he extended the Einstein equation by incorporating binary hydrodynamic interactions between hard spheres [Batchelor, 1977]. The resulting equation contains an additional second order term as given in Equation (2.2),

$$\frac{\eta_0}{\eta_s} = 1 + 2.5\phi + 5.9\phi^2 \quad (2.2)$$

At much higher volume fraction ranging from 0.2 to 0.63, the relative viscosity of hard sphere suspensions can be adequately described by the Krieger- Dougherty (K-

D) model (Equation (2.3)), where the intrinsic viscosity, $[\eta]$ is 2.5 dl/g and maximum volume fraction, ϕ_m is 0.63 for hard spheres [Krieger et al., 1959].

$$\frac{\eta_0}{\eta_s} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (2.3)$$

2.2.2 SHEAR THINNING

Figure 2.1 shows that for $\phi > 0.20$, the viscosity becomes sensitive to shear rate (or equivalently, to shear stress). This shear-rate-dependence of the viscosity occurs when the shear rate is high enough to perturb equilibrium of the distribution of inter-particle spacing.

Brady and co-workers [Bossis and Brady, 1989 ; Phung et al., 1996 ; Brady, 1996] have shown that the Brownian contribution to the shear stress disappeared at high shear stress, leaving only the hydrodynamic contribution. The disappearance of the Brownian contribution led to a viscosity reduction of about a factor of ten for $\phi = 0.2$ in three dimensions, which is in good agreement with experiments.

Light scattering studies on "hard sphere" suspensions are consistent with "string" formation [Ackerson and Pusey, 1988]. The structure of a sheared hard-sphere suspension appears to be similar to that found in simulations of small-molecule liquids at very high shear rates [Hanley et al. 1983]; which also exhibit shear-thinning behavior.

Figure 2.1 The shear rate dependence of the apparent relative viscosity, η_{RA} = suspension viscosity / plastisizer viscosity, of flocculation stable plastisols at dilute through intermediate volume fractions. η_r = suspension viscosity / supernatant viscosity after centrifugation (dashed line) [Bossis and Brady, 1989].

Theoretical investigations [Krieger, 1963] of particle collision dynamics have identified the dimensionless group, the Peclet number Pe , which is defined as;

$$Pe \equiv \frac{\eta_s \dot{\gamma} a^3}{k_B T} \propto \dot{\gamma} t_D \quad (2.4)$$

as the appropriate scaling parameter for describing the importance of Brownian diffusion and shearing forces. The Peclet number expresses the ratio between the hydrodynamic forces due to shear and the Brownian forces, which tend to restore the equilibrium configuration. Peclet number includes effects of the continuous phase viscosity, η_s , particle radius, a , the shear rate, $\dot{\gamma}$, the time taken for the particle to diffuse a distance equal to its radius, t_D and thermal motion.

Figure 2.2 Relative viscosity versus dimensionless shear rate for sterically stabilized monodisperse suspensions of polyvinyl chloride spheres PVC at $\phi = 0.20$. Open symbols (PVC-A, $a=293$ nm); half-filled (PVC-B, $a=619$ nm); solid symbols (PVPVC-C, $a=1154$ nm) [Willey et al., 1978].

Figure 2.2 shows that for three different particle radius: 293, 619 and 1154 nm, the relative viscosity η_r versus Pe curve should be universal for suspensions of monodisperse hard spheres with a fixed volume fraction. The relative viscosities measured over a range of shear rates at a particular volume fraction, but with several particle radius and fluid viscosities, superimpose when plotted against the dimensionless shear rate $\dot{\gamma}_r = 6\pi\eta_0 a^3 \dot{\gamma} / kT$ (Figure 2.2) demonstrates conclusively that only Brownian and viscous forces affect the mechanics. Below volume fractions of 0.2, no shear-thinning was detected while at 0.5 the viscosity in the low-shear limit was about twice that in the high-shear limit [Willey et al., 1978].

2.3 THE RHEOLOGY OF DILUTE POLYMER SOLUTIONS

2.3.1 INTRINSIC VISCOSITY AND OVERLAP CONCENTRATION

The dilute solution viscosity of colloids is a very important parameter that enables the characterization of the molecular dimension. Two commonly used apparatus for dilute-solution viscosity measurement are the Ostwald viscometer and Ubbelohde viscometer (Suspended Level Viscometer). The latter has the advantage that the measurement is independent of the amount of solution in the viscometer and measurements at a series of concentrations can be easily made by successive solvent dilutions.

A parameter of considerable importance is the viscosity ratio or relative viscosity, η_r which is defined as (η/η_s) , and which can be related to the flow time, t and t_s by the relationship:

$$\eta_r \equiv \frac{\eta}{\eta_s} = \frac{t\rho}{t_s\rho_s} \quad (2.5)$$

where t is the time of flow of the liquid (efflux time) through the capillary and ρ is the density of the liquid. Since the difference between the flow times of the solution and pure solvent are of interest, the subscript “s” is used to designate the solvent.

This equation can be further simplified since for a dilute solution $\rho \cong \rho_s$ and so η_r is normally taken as t/t_s . Since η_r becomes unity for an infinitely dilute solution, it is more useful to define the specific viscosity, η_{sp} , which is given by;

$$\eta_{sp} = (\eta_r - 1) = \frac{(t - t_s)}{t_s} \quad (2.6)$$

The specific viscosity corresponds to the fractional increase in viscosity of the solvent due to the presence of polymer molecules. It is obvious that this increase in viscosity will depend on the concentration of polymer molecules in the solution. It is possible to describe the variation of specific viscosity with concentration as the viscosity number or reduced viscosity, (η_{sp}/c) . In addition, the variation of relative viscosity with concentration is described as the inherent viscosity, $(\ln \eta_r/c)$. When the solution concentration approaches zero, both the reduced and inherent viscosities approach the intrinsic viscosity;

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{\ln \eta_r}{c} \quad (2.7)$$

where $[\eta]$ is the intrinsic viscosity and c is the concentration of the polymer solution. The intrinsic viscosity $[\eta]$, which for suspensions is the dilute limit of the viscosity increment per unit particle volume fraction, divided by the solvent viscosity. It describes the ability of the polymer molecules to increase the viscosity of the solvent in the absence of any inter-molecular interactions.

For polyelectrolytes [Guo, 1997; Kjoniksen et al., 1997; Kumacheva et al., 1997; Ng et al., 1999], where ionic charges are present, the polymer is very sensitive to the salting effect in solution. Therefore, the determination of intrinsic viscosity of polyelectrolytes at low salt concentrations is more complicated compared to the non-ionic polymers due to two opposing effects; i.e., the Coulombic repulsive forces between similar ionic charges and the attractive interactions between the hydrophobic segments. Due to the presence of polyelectrolyte effect, which alters the polymer-

solvent interactions, and hydrodynamic volume of polymer chains, the intrinsic viscosity can either be determined at high concentrations of salt or at controlled conductivity environment at different polymer concentrations.

Ng et al. studied the effects of ionic strength on the intrinsic viscosity measurements of hydrophobically modified alkali-swelling emulsion (HASE). The ionic strength of the dilute polymer solution was found to influence the degree of hydrophobic association and the size of micellar cluster during dilution. The variation of the above factors was experimentally found to have significant effects on the accuracy, reliability and repeatability of the intrinsic viscosity and Huggins coefficient. Hence, constant ionic strength of the solvent must be maintained so that accurate data can be determined (Ng et al., 1999).

2.4 ELECTRICALLY CHARGED PARTICLES

2.4.1 PARTICLE CHARACTERIZATION

A common method of stabilizing particle suspensions is through electrostatic charging of particle surfaces. The charges lead to long-range repulsions that maintain the particles at a sufficient distance so that they are not drawn together by short-range van der Waals forces. Because electrostatic interactions are long-ranged, strong electrostatic effects are possible even at minute particle volume fractions, as low as $\phi \approx 0.001$.

Two spherical particles whose centers are separated by a distance r repel each other with an interaction potential $W(r)$ of

$$W(r) = 2\pi\epsilon\epsilon_0 a \psi_s^2 \ln[1 + \exp(-\kappa(r - 2a))] \quad (2.8)$$

where ψ_s is the surface potential of the particles, $\epsilon_0 = 8.8 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1}$ is the permittivity of space, ϵ is the dielectric constant, a is the particle radius, and κ^{-1} is the Debye length. Equation (2.8) is valid for constant surface potential when $\kappa D \leq 2$ where $D = r - 2a$. For particles with large inter-particle separation, where $\kappa D \geq 2$, Equation (2.8) is replaced by the following:

$$\frac{W(r)}{k_B T} = \frac{\alpha \exp(-\kappa r)}{\kappa r} \quad (2.9)$$

and

$$\alpha \equiv \frac{4\pi\epsilon\epsilon_0 \psi_s^2 a^2 \kappa \exp(2\kappa a)}{k_B T} \quad (2.10)$$

Since the long range forces keep particles apart, the *surface charges increase the effective particle diameter*. The effective particle diameter d_{eff} can be estimated from:

$$W(r = d_{\text{eff}}) \approx k_B T \quad (2.11)$$

This condition, when applied to Equation (2.9) for the low-salt case, gives,

$$d_{\text{eff}} \approx \frac{1}{\kappa} \ln(\alpha / \ln[\alpha / \ln(\alpha / \dots)]) \quad (2.12)$$

The effective volume fraction of particles is, therefore $\phi_{\text{eff}} \equiv \phi (d_{\text{eff}}/2a)^3$. Since a hard-sphere suspension forms a macro-crystalline lattice at a volume fraction of around $\phi \approx 0.55$, charged spheres will do so when:

$$\phi_{\text{eff}} \equiv \phi \left(\frac{d_{\text{eff}}}{2a} \right)^3 \quad (2.13)$$

is greater than around 0.55. At low ionic strength, $d_{\text{eff}} \gg 2a$; thus charged colloids can form iridescent, macro-crystalline phases at very low particle volume fractions.

2.4.2 VISCOSITY

The effective enlargement of the diameter of charged spheres as shown in Equation (2.12) leads to enhancement of the low-shear-rate viscosity. According to Russel [Russel, 1980; Russel et al., 1989], the dependence of zero-shear viscosity up to second order in ϕ of a disordered suspension of charged spheres is:

$$\frac{\eta}{\eta_s} = 1 + 2.5\phi + \left[2.5 + \frac{3}{40} \left(\frac{d_{\text{eff}}}{a} \right)^5 \right] \phi^2 \quad (2.14)$$

where d_{eff} is given by Equation (2.12). For ϕ_{eff} greater than 0.10, η/η_s can be predicted by extending the Krieger-Dougherty equation,

$$\frac{\eta}{\eta_s} = \left(1 - \frac{\phi_{\text{eff}}}{\phi_m} \right)^{-(5/2)\phi_m} \quad (2.15)$$

For aqueous polystyrene latices at high ionic strengths or low surface charge densities, Krieger and coworkers reported for volume fractions as high as 0.50 that only moderate shear-thinning with well-defined Newtonian high- and low-shear limits was observed [Krieger, 1972 and Krieger et al., 1976]. Subsequent reduction in the ionic strength, which extends the range of electrostatic repulsions between particles, caused a dramatic increase in the viscosities at low shear rates, eventually producing an apparent yield stress or infinite zero-shear viscosity (Figure 2.3). As the shear rate increases, the hydrodynamic contributions to the viscosity increase, whereas the electrostatic contribution to the viscosity shear-thins until the viscosity is close to that expected for uncharged particles [Russel, 1980].

Figure 2.3 Effect of added electrolyte on the relative viscosity of polystyrene latex suspension with diameter of 0.11 μm at $\phi = 0.40$. $\circ$: Deionized; $\square$: 1.876×10^{-4} M HCl; $\blacksquare$: 1.876×10^{-3} M; $\blacktriangle$: 9.378×10^{-2} M; $\bullet$: 1.876×10^{-2} M [Russel, 1980].

2.5 SOFT SPHERE COLLOIDAL PARTICLES

The above review indicates tremendous progress made concerning the rheology of hard sphere systems, both experimentally as well as theoretically. This has motivated scientists and rheologists to develop and extend these models to various hard sphere suspensions coated with a soft polymeric layer and stimuli-responsive microgels. The later part of this chapter discusses the characteristics of stimuli-responsive microgels and examines the advantages and limitations of various attempts to model the behavior of soft condensed particles.

2.5.1 CHARACTERISTICS OF MICROGELS

A microgel is an intra-molecularly cross-linked macromolecule, which is dispersed in solvent, and the degree of swelling depends on the degree of cross-linking and the nature of the solvent [Wolfe et al., 1989; Rodriguez et al., 1992; Bartsch et al., 1997; Funke et al., 1998]. Besides linear and branched macromolecules and cross-linked polymers, intra-molecularly cross-linked macromolecules (microgels) may be considered as a fourth class of macromolecules.

Due to the compact structure of microgels, their intrinsic viscosities, $[\eta]$ are much smaller than those of corresponding linear or branched polymers. In Figure 2.4, $[\eta]$ of copolymer divinyl benzene (DVB) and styrene (S) cross-linked with divinyl monomer (DVM) is plotted against their cross-linked density (mole % DVM). The experimental

data points were taken from different sources [Shashoua et al., 1958; Sieglaff, 1963; Hoffmann, 1974; Antonietti et al., 1990; Bolle, 1993]. They found a reverse proportionality of $[\eta]$ of cross-linked DVB/S to the molar ratio of cross-linker, DVM. This reflects the initial rapid decrease in size of a swollen microgel with increasing cross-linked density up to about 3 mole% of cross-linking monomer content, and finally $[\eta]$ attains a limiting value of 4 mL/g which is somewhat higher than the value of 2.5 mL/g for rigid spheres determined from the Einstein equation.

Figure 2.4 Variation of the $[\eta]$ of microgels formed by emulsion polymerization with the amount of divinyl monomer (DVM) in the monomer mixture. The experimental data points were taken from following sources:

- (●): Shashoua, 1958; technical-DVB/S microgels; measurements in benzene at 30°C.
- (○): Sieglaff, 1963; technical-DVB/S microgels; measurements in toluene at 25°C.
- (▲): Hofmann, 1974; technical-DVB/S microgels; measurements in salt-containing DMF at 25°C.
- (△): Antonietti, 1990; 1,3-diisopropenylbenzene/S microgels; measurements in toluene at 20°C.
- (▼): Bolle, 1993; 1,4-DVB/S microgels; measurements in toluene at 25°C.

2.5.2 SWELLING AND ELASTICITY OF STIMULI-RESPONSIVE MICROGEL

The mechanism of swelling of microgel particles containing pH-responsive groups is governed by the internal osmotic pressure due to the mobile counter-ions contained within the particles which balances the internal electrostatic repulsion [Saunders et al., 1999]. The equation of swelling of microgels is determined by the balance between the osmotic pressure inside the microgels and the osmotic pressure outside, as described by Equation (2.16):

$$\Pi_{\text{in}} + \Pi_{\text{el}} = \Pi_{\text{out}} \quad (2.16)$$

where Π_{in} and Π_{out} are respectively the osmotic pressure of the mobile ions inside the microgels and bulk solution [Cloitre et al., 2003]. Π_{el} is the elastic pressure of the polymeric network described by Equation (2.17):

$$\Pi_{\text{el}} = -\frac{RTc_0}{2N_x Q^{1/3}} \quad (2.17)$$

where $Q = (R_\alpha / R_{\alpha=0})^3$ is the swelling ratio of microgels, N_x the cross-linked density and c_0 the polymer concentration in the particles at collapsed state. R_α represents the hydrodynamic radius of the particle at a particular α and $R_{\alpha=0}$ represents the hydrodynamic radius of the unneutralized ($\alpha=0$) particle, both measured using dynamic light scattering technique. The terms Π_{in} and Π_{out} can be described by:

$$\Pi_{\text{in(out)}} = RT C_{\text{in(out)}} \quad (2.18)$$

where C_{in} and C_{out} are the concentrations of the ions inside and outside the microgels.

Recently, Cloitre and co-workers showed that the theoretical prediction of relative swelling of polyelectrolyte microgel agreed with experimental data [Cloitre et al., 2003]. In the absence of salt, i.e. $C_{\text{out}} = 0$, all the counter-ions associated with the ionized units are trapped inside the polymeric network by the electrostatic attraction exerted by the fixed charges, $C_{\text{in}} = \alpha c_0 y / Q$ where c_0 is the polymer concentration inside the particles at collapsed state, y is the molar fraction of acidic units and α is the neutralization degree. By combining Equations (2.16) to (2.18), the swelling ratio Q of the microgels as a function of neutralization degree, α and cross-linked density, N_x can be described by the scaling relation below,

$$Q \propto (\alpha N_x)^{3/2} \quad (2.19)$$

which assumes that all the counter-ions are trapped inside the microgels.

Figure 2.5 (a) variation of the swelling ratio at maximum swelling versus the cross-linked density. (b) variation of the swelling ratio with the neutralization degree for $N_x=140$ (●), $N_x=70$ (◆), $N_x=28$ (▲) [Cloitre et al., 2003].

Wolfe and Rodriguez studied the changes in the internal polymer segment density and particle swelling during the alkalization of internally cross-linked methacrylic acid-ethyl acrylate (MAA-EA) microgels using static and dynamic light scattering [Rodriguez et al., 1994]. Upon neutralization with a base, pronounced negative deviations of the ratio of the radius of gyration, R_g to hydrodynamic radius, R_h , from the known value for homogeneous spheres along with the curvature in Guinier plots of the angular dependent light scattering intensity indicated a non-uniform polymer segment density distribution within the microgels [Wolfe et al., 1989; Antonietti et al., 1990; Nerger et al., 1979].

2.5.3 APPROACH TO MODEL SOFT PARTICLES

In the last 15 years, significant progress was made where theoretical and semi-empirical models were developed and extended to various hard sphere suspensions coated with a soft polymeric layer and stimuli-responsive microgels [Krieger, 1959, 1972; Batchelor, 1977; Werff et al., 1989; Onoda et al., 1990; Brady, 1993; Lionberger et al., 1994; Shikata et al., 1994; Meeker et al., 1997; Horn et al., 2000]. Some progress was made but a universal expression to describe the behavior of soft condensed particles is still elusive.

Perhaps the most significant contribution in the field of stimuli-responsive microgels can be attributed to the pioneering work of Ballauff and Richtering [Senff et al., 1999; Senff et al., 2000; Ballauff, 2003]. They reported the behavior of thermo-sensitive core-shell particles with a mono-dispersed polystyrene (PS) grafted with a layer of cross-linked poly(N-isopropyl acrylamide) (PNIPAM) and a pH-responsive shell consisting of polyacrylic acid. A simple method for treating the viscosity data was to determine the effective volume fraction of particles, where the volume fraction ϕ was replaced by the effective volume fraction ϕ_{eff} using the Batchelor equation for hard sphere as shown in Equation (2.20),

$$\frac{\eta_0}{\eta_s} = 1 + 2.5\phi_{\text{eff}} + 5.9\phi_{\text{eff}}^2. \quad (2.20)$$

The effective volume fraction ϕ_{eff} can be substituted by the term kc , where c is the mass concentration of the dispersion in g/ml and k is the specific volume in ml/g to convert the mass concentration to the effective volume fraction. Hence, Equation (2.20) can be rewritten as,

$$\frac{\eta_0}{\eta_s} = 1 + 2.5(kc) + 5.9(kc)^2 \quad (2.21)$$

where the constant k is the only adjustable parameter.

The relative viscosity of dilute PNiPAM microgel solutions is shown in Figure 2.6 as a function of the mass concentration, c for different temperatures. The lines represent fits according to Equation (2.21) with the effective volume fraction ϕ_{eff} substituted by $\phi_{\text{eff}} = kc$. Strong temperature dependence is evident, which is caused by the shrinkage of the particles.

Figure 2.6 η_0/η_s of PNiPAM particles at different temperatures versus polymer concentration in weight percent. The lines display fits according to Equation (2.21) [Senff et al., 2000].

The relative viscosity of PNIPAM microgel dispersion was plotted against ϕ_{eff} calculated from the constant k determined from Equation (2.21). All the data determined at different temperatures seemed to fall into a single master-curve, which is consistent with the hard sphere prediction from Equation (2.20) for ϕ_{eff} up to 0.1

[Senff et al., 1999; Senff et al., 2000; Ballauff, 2003]. Beyond ϕ_{eff} of 0.1, the data deviated from the prediction of the modified Batchelor equation (Equation (2.20)), and this was attributed to the particle-particle repulsion. The deviation from the Batchelor prediction suggests that the specific volume, k obtained at dilute solution regime is not representative of the “true” effective volume of soft particles in regions where inter-particle repulsion is present.

This phenomenon becomes even more apparent when the Krieger-Dougherty (K-D) model (Equation (2.3)) was used to predict the relative viscosity of concentrated suspensions. Richtering and co-workers [Senff et al., 1999; Senff et al., 2000] determined a constant k value for PNIPAM at each temperature and used the modified Krieger Dougherty model shown in Equation (2.22) to predict the observed relative viscosity.

$$\frac{\eta_0}{\eta_s} = \left(1 - \frac{k\phi}{\phi_m} \right)^{-[\eta]\phi_m} \quad (2.22)$$

Another major contribution was credited to Cloitre and co-workers [Cloitre et al., 2003] where they successfully computed the volume fraction of pH responsive microgels using the values calculated in Equation (2.19) for the swelling ratio. The Debye length associated with the counter-ions at concentration C_{in} was compared with the characteristic size of the microgels:

$$\kappa_{\text{in}}^{-1} = (4\pi l_B N_A C_{\text{in}})^{-1/2} \quad (2.23)$$

where l_B is the Bjerrum length and N_A the Avogadro number. Only counter-ions in a peripheral shell of thickness κ_{in}^{-1} can leave the microgels and diffuse in the solution and the fraction of those counter-ions is:

$$\Gamma \cong 3\kappa_{\text{in}}^{-1} / R_h \quad (2.24)$$

At a higher microgel concentration, the concentration of free counter-ions in the solution can be large enough to induce an osmotic de-swelling of the microgels and this phenomenon can be quantified using Equations (2.16) to (2.18) where C_{in} and C_{out} now take into account the existence of free counter-ions. The new expressions for C_{in} and C_{out} are given below [Borrega et al., 1999]:

$$C_{\text{in}} = \alpha(1 - \Gamma)yc_0 / \tilde{Q} \quad \text{and} \quad C_{\text{out}} = \alpha\Gamma yc_0 \phi / \tilde{Q}(1 - \phi) \quad (2.25)$$

where $\tilde{Q}$ is the swelling at finite concentration and ϕ is the volume fraction of microgels in the solution. Solving Equations (2.17), (2.18) and (2.25), the expression for the swelling ratio at finite concentration, $\tilde{Q}$, as a function of the swelling ratio at infinite dilution Q is described by:

$$\frac{\tilde{Q}}{Q} = \left[1 - \frac{\Gamma}{1 - \phi} \right]^{3/2}. \quad (2.26)$$

The volume of microgels can reduced by one third near close packing ($\phi = 0.6$) and thus osmotic de-swelling has important consequences on the flow behavior of microgels at high concentration. The mass concentration, c of the dispersion in g/ml and ϕ are related through the simple relation:

$$\phi = \frac{\tilde{Q}}{V_m c_0} \frac{\rho_s}{\rho_p} c \quad (2.27)$$

where V_m is the molar volume of monomeric units, ρ_s and ρ_p are the specific mass of the suspension and polymer respectively. The volume fraction of microgels can be

easily computed using the values calculated for the swelling ratio. Cloitre and co-workers [Cloitre et al., 2003] investigated microgels with different cross-linking density and showed that the data collapsed nicely on a single curve, which is very close to the analytical form expected for polydisperse hard sphere [Werff, 1994], $\eta_0/\eta_s = (1 - \phi/\phi_m)^{-2}$. They emphasized that it is crucial to use $\tilde{Q}$ to calculate the volume fraction of microgels whereas using Q would lead to an overestimation of the volume fraction by a large factor.

2.6 STORAGE AND LOSS MODULUS

Another way to explore rates of structural rearrangement within a complex fluid is to impose small-amplitude oscillatory shearing, which does not significantly deform the fluid's microstructure. This kind of deformation can be achieved in a cone-and-plate geometry by rotating the cone about its axis with an angular velocity that oscillates sinusoidally, $\Omega(t) = \Omega_0 \cos(\omega t)$, where ω is the frequency of oscillation, in units of radians per second. The shear rate is also a sinusoidal function of time, $\dot{\gamma}(t) = \Omega / \tan \alpha = \Omega_0 \cos(\omega t) / \tan \alpha$, and so is the shear strain γ , which is the time integral of the shear rate, $\gamma = (\Omega_0 / \omega) \sin(\omega t) / \tan \alpha$. The ratio (Ω_0 / ω) is the amplitude of the angular deflection of the cone, and $\gamma_0 = (\Omega_0 / \omega) / \tan \alpha$ is the strain amplitude imposed on the fluid. In a plane Couette geometry, the strain amplitude is the amplitude of the displacement of the sliding plate, divided by the gap.

If the strain amplitude γ_0 is small enough (typically $\gamma_0 \ll 1$) that the fluid structure is not significantly disturbed by the deformation, then the stress measured during the oscillatory deformation is controlled by the rates of spontaneous rearrangements, or relaxations present in the fluid in the quiescent or equilibrium state. The shear stress $\tau(t)$ produced by a small amplitude deformation is proportional to the amplitude of the applied strain γ_0 and is itself sinusoidally varying in time. In general, the sinusoidally varying stress can be represented as:

$$\tau(t) = \gamma_0 [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)] \quad (2.28)$$

The term $G'(\omega)$ is called the *storage modulus*, while the term $G''(\omega)$ is called the *loss modulus*. The storage modulus represents storage of elastic energy, while the loss modulus represents the viscous dissipation of that energy. The ratio G''/G' , which is called the loss tangent $\tan(\delta)$, is high ($\gg 1$) for materials that are liquid-like, but is low ($\ll 1$) for materials that are solid-like.

The storage and loss modulus, G' and G'' for "liquid-like" and "solid-like" fluids are shown in Figure 2.7. For the "liquid-like" fluid, the storage modulus is much lower than the loss modulus, and it scales with frequency as $G' \propto \omega^2$, the loss modulus is linear in frequency, $G'' \propto \omega$. The low-frequency "liquid-like" region in which G' and G'' obey these power laws is called the terminal region. For the "solid-like" fluid, $G' \gg G''$, and G' is nearly frequency-independent.

Figure 2.7 Illustration of frequency-dependent storage and loss modulus, G' and G'' for a typical "liquid-like" and "solid-like" materials.

Microgel dispersions often show behavior intermediate to the "solid-like" and "liquid-like" prototypes. When the zero-shear viscosity diverges, the microgel particles come into close contact and elastic properties of the densely packed spheres arise.

Richtering and co-workers [Senff et al., 1999; Senff et al., 2000] measured the yield stress and the elastic modulus of concentrated poly(N-isopropyl acrylamide) (PNIPAM) suspensions and these properties are a function of temperature for a given volume fraction. The yield stress for 2wt% cross-linked PNIPAM at microgel concentration of 6.8wt% is shown in Figure 2.8. At low temperatures, the sample behaved as a viscoelastic solid, i.e. the storage modulus was higher than the loss modulus in the whole frequency range. G' was independent of the frequency and corresponds to the plateau modulus, G_p .

Figure 2.8 Yield stress for 2wt% cross-linked PNIPAM at microgel concentration of 6.8wt%: shear rate (filled symbols) and strain (open symbols) as a function of the shear stress for different temperatures [Senff et al., 1999].

Upon heating, the sample changed to a viscoelastic liquid with $G'' > G'$ (Figure 2.9).

G_p decreased with temperature and a master-curve was obtained when G_p was plotted versus ϕ_{eff} (Figure 2.10).

Figure 2.9 Elastic modulus, G' (filled symbols) and loss modulus, G'' (open symbols) versus frequency for 4wt% cross-linked PNIPAM at microgel concentration of 7.15 wt% and temperatures, $\blacksquare$: 10 °C ; $\blacktriangle$: 20 °C and $\blacklozenge$: 30 °C [Senff et al., 1999].

Figure 2.10 Double-logarithmic plot of the plateau modulus against the effective volume fraction for 4wt% cross-linked PNIPAM with a power-law fit [Senff et al., 1999].

The elastic plateau modulus can be related to the interaction potential and the pair correlation function using the Zwanzig and Mountain equation [Wagner, 1993; Bergenholtz et al., 1998],

$$G_p = nkT + \frac{2\pi}{15} n^2 \int_0^\infty g(r) \frac{d}{dr} \left(r^4 \frac{d\psi}{dr} \right) dr \quad (2.29)$$

Here n is the particle number density, k is the Boltzmann constant, and $g(r)$ is the radial distribution function with r the center-center separation, and $\psi(r)$ the pair interaction potential. Assuming a lattice-like microstructure, a simple expression can be obtained,

$$G_p \propto \frac{I}{r} \left(\frac{\partial^2 \psi}{\partial r^2} \right) \quad (2.30)$$

The inter-particle distance r can be related to the volume fraction at closed packing as

$$r^3 = (2a)^3 \frac{\phi_{\text{eff,max}}}{\phi_{\text{eff}}} \quad (2.31)$$

and the effect of temperature-dependent swelling on the modulus is canceled out when the ϕ_{eff} is used as the concentration variable. Wagner pointed out that Equation (2.30) is obtained when the hydrodynamic interaction is neglected, whereas taking into account hydrodynamic interaction leads to a more complicated expression, which also includes the first derivative of $\psi(r)$ [Wagner, 1993]. Nevertheless, Equation (2.30) provides a good fit to experimental data in Figure 2.10, probably due to a cancellation of errors when a lattice-like structure is assumed and hydrodynamic interactions are neglected.

Paulin et al. modeled the interaction potential of concentrated microgel dispersions as $\psi(r) \propto 1/r^n$, which gives a power law behavior for the concentration dependence of

the plateau modulus, $G_p \propto \phi_{\text{eff}}^m$ [Paulin, 1996]. The temperature sensitive PNIPAM microgels exhibit a linear relationship in a double-logarithmic plot of G_p versus the effective volume fraction with a power law exponent of 5.7 (Figure 2.10). Paulin et al. investigated poly (methyl methacrylate) microgels and found a power law exponent of 7.7 [Paulin, 1996]. The exponent may be compared to results obtained by Liang et al. from latices sterically stabilized with short poly(ethylene oxide) chains, who found much higher exponents [Liang et al., 1995].

The power-law exponent, m , of the plateau modulus is related to the exponent, n , of the interaction potential via $m = 1 + n/3$. Thus the slope of G_p in Figure 2.10 corresponds to $n = 14.5$ and indicates soft sphere behavior. A higher cross-linked density leads to a higher inter-particle force as determined by the elastic properties.

2.7 STATIC STRUCTURE FACTOR

When there is interaction between the particles, the positions of neighbouring particles become correlated and can therefore give rise to diffraction patterns. Under certain conditions, the study of inter-particle scattering can yield information about the structure of a liquid or colloidal system, which can be used to corroborate the particle interaction potential as obtained from the rheometry technique.

In most experimental situations, it can be assumed that the scattering process only changes the direction and not the energy or frequency of the radiation. This assumption (of elastic energy) is valid if the energy of the radiation is much larger than the average kinetic energy of the scattering particle i.e. $h\nu \gg kT$, so that there is negligible energy lost to or gained from the scatterers. Furthermore, in order to be able to analyze the scattering pattern, the concentration of scattering particles must be ‘sufficiently’ dilute so that the incident radiation only experiences a single scattering event before reaching the detector.

The general results for the average scattered intensity from particles of finite size should have the following relationship,

$$\langle I_s \rangle = \text{constant} \times f(\theta) \times P(Q) S(Q) \quad (2.32)$$

where $f(\theta)$ depends on the polarization of the incident and scattered radiation. The *form factor* $P(Q)$ is a property of the shape and size of the scattering particle. The *(static) structure factor* $S(Q)$ is proportional to the susceptibility $\tilde{\chi}(Q)$, which characterizes the density, ρ response of the system to external perturbation of spatial

frequency Q or wavelength $\lambda = 2\pi/Q$. In the dilute limit ($\rho \rightarrow 0$) we have $S(Q)=1$ and this limit is used to determine the prefactors of $S(Q)$ which are independent of number density [Hunter, 1991].

As $Q \rightarrow \infty (\lambda \rightarrow 0)$, the wavelength will become much smaller than the inter-particle spacing and the external field would have undergone many oscillations between every pair of particles. Consequently, there can be no correlations in the local density in response to such perturbation, as each particle is in effect subject to uncorrelated perturbations. If light scattering is carried out to measure the colloid structure factor $S(Q)$ of a dispersion, an extrapolation to $Q = 0$ will yield the value of the osmotic compressibility, κ_T [Ottewill, 1982],

$$S(Q=0) = \rho k T \kappa_T = k T (\delta \rho / \delta p)_T. \quad (2.33)$$

A colloidal dispersion is defined as concentrated if its properties are influenced by interactions between the constituent particles. An estimation on the magnitude of the effect of this interaction can be obtained by computing the osmotic compressibility, κ_T . The osmotic compressibility, κ_T , is a measure of the resistance of the dispersion to any attempt to squeeze its particles closer together, and anything which increases that resistance will lower the compressibility. Clearly, adding a repulsive potential has this effect and the longer the range of the potential, the lower the density at which the compressibility will begin to diminish. Imagine first starting with a hard-sphere system, in which the range of the interaction is the diameter, d , of the spheres. From the above discussion, this system is expected to exhibit features associated with concentrated behavior once the mean spacing between particles, δ becomes comparable with the range of the potential, or when $\delta/d \sim 1$. Now for sphere that

possesses a charge, for example by ionization, the resulting total ionic strength of the particles suspension corresponds to a Debye screening length, κ^{-1} . In this case, the onset of concentrated behavior will occur when $(\delta - 2\kappa^{-1})$ becomes comparable with the range of the potential, or when $(\delta - 2\kappa^{-1})/d \approx 1$. In this case, the suspension show concentrated behavior, even though the mean spacing between particles, δ is larger and it contains lower number of particles.

Since charged particle offer finite resistance to being squeezed together, they are often referred to as a “soft sphere” system. More formally, the osmotic compressibility, κ_T , is expected to be smallest for small inter-particle separations. In contrast, in a neutral system where excluded volume effects dominate, contact is the most likely configuration, because it is the only time the particles are aware of a neighbouring particle, and the collision of particles can be induced by the thermal energy. Therefore, κ_T for hard spheres is greatest at small distances [Hunter, 1991]. We see that the effective hard sphere models are generally not useful when discussing soft-sphere systems because the two systems show fundamentally different characteristics in the osmotic compressibility functions.

2.7.1 TURBIDIMETRY TO DETERMINE STRUCTURE FACTOR

Turbidimetry provides a means to obtain the long wavelength portion (λ) of the structure factor of colloidal suspensions. This method is practically insensitive towards multiple scattering, unlike the light scattering technique. Therefore it is well suited for studying concentrated, strongly turbid systems where multiple scattering prevails [Apfel, 1994; Apfel, 1995; Horner, 1997].

The turbidity τ is defined as the attenuation (weakening) of a light beam by scattering when passing through a sample. Thus,

$$\tau = l^{-1} \ln(I_0/I_t) \quad (2.34)$$

with I_0 being the incident intensity of the light, I_t the transmitted intensity and l the length of the optical path. When absorption can be excluded, the intensity of the scattered light and the turbidity are related through the following relation:

$$\tau = 2\pi \int_0^\pi R(q) \sin\theta \, d\theta \quad (2.35)$$

where $R(q)$ is the Rayleigh ratio for unpolarized light, $q = (4\pi n_0/\lambda_0) \sin(\theta/2)$ is the magnitude of the scattering vector, θ the scattering angle, n_0 the refractive index of the medium and λ_0 the wavelength in vacuo. It is assumed that the size parameter $n_0\pi d/\lambda_0$ with d being the diameter of the particles, is below unity. Therefore, it is permissible to use the Rayleigh-Debye (RD) theory for the theoretical evaluation of turbidity [Kerker, 1969]. Since the relative refractive index $m = n_p/n_0$ where n_p the refractive index of the immersed particles, is considerably higher than 1, the Lorenz-

Lorentz factor $\left(m^2 - 1\right) / \left(m^2 + 2\right)$ is not replaced by $(2/3)(m - 1)$ as is usually done within the RD approximation. Thus, the main error of the RD theory in this range of the size parameter $n_0 \pi d / \lambda_0$ is avoided and the RD expressions are expected to provide a very good approximation [Kerker, 1969].

The Rayleigh ratio, $R(q)$ is defined as

$$R(q) \propto c P(q) S(q, \phi) \quad (2.36)$$

where c and ϕ is the mass concentration and volume fraction of the colloidal particles respectively. In the region of low qR , $P(q)$ and $S(q, \phi)$ can be approximated by [Hunter, 2001]

$$P(q) = 1 - \frac{1}{3}(qR)^2 + O(q^4 R^4) \quad (2.37)$$

and

$$S(q, \phi) = S(0, \phi) + \gamma (qR)^2 + O(q^4 R^4) \quad (2.38)$$

where γ is a constant. Ballauff et al. [Apfel, 1995 ; Weiss, 1996 ; Horner, 1997] tested these approximations by comparing the integrated structure factor calculated using the above approximations with the exact result obtained by integrating Equation (2.35) with the Percus-Yevick structure factor. The calculations were carried out for 120 nm diameter hard spheres, and there was good agreement between both methods for wavelengths greater than 500 nm. Insertion of Equations (2.37) and (2.38) into $R(q)$ and subsequent integration of Equation 2.35 leads to

$$\tau \propto c Q(\lambda^2) Z(\lambda^2, c) \quad (2.39)$$

where $Q(\lambda^2)$ is an integrated form factor and $Z(\lambda^2, c)$ is the integrated structure factor,

$$Z(\lambda^2, c) = S(0, c) + O(1/\lambda^2) \quad (2.40)$$

In the region of low concentrations, $Z(\lambda^2, c) \rightarrow 1$ (inter-particle interferences are negligible). Hence,

$$\left(\frac{\tau}{c}\right)_{c=0} \propto Q(\lambda^2) \quad (2.41)$$

and

$$Z(\lambda^2, c) = \frac{(\tau/c)}{(\tau/c)_{c=0}} \quad (2.42)$$

Equation (2.42) suggests that $Z(\lambda^2, c)$ can be calculated from a plot of (τ/c) as a function of c at fixed λ by division of the (τ/c) values when the concentration is extrapolated to zero. A plot of $Z(\lambda^2, c)$ as a function of $1/\lambda^2$ is then made. The intercept of this plot at each concentration is the structure factor $S(0)$, which is proportional to the osmotic compressibility, κ_T from Equation (2.33).

2.8 SUMMARY

Our literature review demonstrates that significant progress has been made where theoretical and semi-empirical models were developed and extended to various soft sphere models. However, a universal expression to describe the behavior of soft condensed particles is still elusive. As a first step towards developing a generalized approach to model soft microgel particles, a wide variety of model soft sphere systems were examined where the characteristics of microgel particles and their corresponding interaction potential was manipulated by varying the following; (a) degree of neutralization, α of MAA groups, (b) salt concentrations, (c) microgel cross-linked density, and (d) molar ratio of MAA-EA. Therefore the microstructural evolution of the microgel systems can be correlated to their bulk rheological behavior. The experimental results provided new physical insights needed for the development of a generalized model. In addition, the validity and limitations of the proposed approach will be examined by comparing these results against a theoretical approach that was reviewed earlier. The review on the structural properties of microgels is of technical importance since they are intimately connected to the particle interaction potentials. Thus, a good understanding of these parameters permits a quantitative evaluation of the factors governing particle osmotic compressibility as well as the flow behavior of these systems.

3 MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 SYNTHESIS OF CROSS-LINKED MAA-EA MICROGELS

Model swellable particles were prepared by Dow Chemicals using the conventional semi-continuous emulsion polymerization of methacrylic acid (MAA) and ethyl acrylate (EA) cross-linked with di-allyl phthalate (DAP). A monomer mixture of total weight of 620g in the desired molar ratios was prepared by charging ethyl acrylate and methacrylic acid (both from Aldrich Chemical Co.), together with a 26g of a 75% solution of Aerosol OT surfactant (American Cyanamid, Stamford, Connecticut), and 60g of distilled de-ionised water to a bottle, and the contents dispersed with vigorous shaking. This monomer mixture was then charged to a 1-litre graduated monomer-feed cylinder.

An initiator feed mixture comprising 8g of sodium persulfate (Aldrich Chemical Co.), 2g of sodium bicarbonate (Aldrich Chemical Co.) and 45g of distilled de-ionised water was prepared in another container, and was charged to a (100-millilitre) syringe pump. In a third container, 16g of sodium persulfate was dissolved in 40g of water to form the initial catalyst solution. To the reaction vessel (a 3-litre resin flask), 1377g of distilled de-ionised water, 5.3g of 2-sulfoethyl methacrylate (Hampshire Chemical Co.) and 5.3g of 75% solution of Aerosol OT surfactant were charged. Under nitrogen purge, the reactor was heated to 80°C, whereupon 68g of the monomer mixture were added.

CHAPTER 3

MATERIALS & EXPERIMENTAL TECHNIQUES

When the reactor temperature reached 80°C, the catalyst solution was added to the reactor to initiate polymerization. After the initial monomers had reacted for 30 minutes to form an in-situ seed product, the remaining monomer and initiator feed mixtures were conveyed to the reaction vessel at a rate of 4.5 and 0.4 g/min, respectively, over a two hour and two-and-a-half hour period, respectively, while the reaction mixture was under continuous stirring at a reaction temperature of 80°C. The reaction was left to proceed for another hour to react residual monomers, after which the solid product was cooled and filtered through a 200-mesh nylon cloth. The final solid content of the polymers was approximately 10% by weight.

The chemical structure of cross-linked MAA-EA microgel used in this study is schematically shown in Figure 3.1(a) and the properties are tabulated in Table 3.1(a). These microgels are designated as HASE-y-x-z, where the subscript y and x correspond to the mole percent of MAA and EA whereas z denotes the weight percent of cross-linker DAP. For example, the microgel with MAA/EA molar ratio of 40:60 and amount of grafted di-allyl phthalate of 4wt% is designated as HASE-40-60-4.

It is also convenient to characterize the cross-linked density by the average number of monomers between two cross-links, N_x . N_x can be calculated by assuming that one cross-link connects two chain segments and that the different monomers are homogenously distributed inside the microgels.

3.2 SYNTHESIS OF CORE-SHELL MICROGELS

Model core-shell pH-responsive microgels consisting of hard PMMA particles, grafted with a soft layer of methacrylic acid-ethyl acrylate (MAA-EA) cross-linked with di-allyl phthalate (DAP), were prepared by Dow Chemicals using the conventional semi-continuous emulsion polymerization. The particles were prepared by charging 4.5g methyl methacrylate (MMA) seed latex of approximate 130 nm in diameter together with a 26g of a 75% solution of Aerosol OT surfactant (American Cyanamid, Stamford, Connecticut), and 415g of distilled de-ionised water to a bottle, and the contents dispersed with vigorous shaking. This monomer mixture was then charged to a 1-litre graduated monomer-feed cylinder. In a second container, 16g of sodium persulfate was dissolved in 40g of water to form the initial catalyst solution. To the reaction vessel (a 3-litre resin flask), 1377g of distilled de-ionised water, 5.3g of 2-sulfoethyl methacrylate (Hampshire Chemical Co.) and 5.3g of 75% solution of Aerosol OT surfactant were charged. Under nitrogen purge, the reactor was heated to 80°C, whereupon 68g of the monomer mixture were added. PMMA particles without the cross-linked MAA-EA shell was also synthesized separately using emulsion polymerization as mentioned above.

The chemical structure of MMA used as the core is schematically shown in Figure 3.1(b) while the cross-linked MAA-EA shell has similar chemical structure as shown in Figure 3.1(a). The properties of this core-shell system are tabulated in Table 3.1(b). These core-shell microgels are designated as CS-y-x-z, where CS represents core-shell while the subscript y and x correspond to the mole percent of MAA and EA whereas z denotes the weight percent of cross-linker DAP present in the shell.

Brookhaven dynamic light scattering system was used to measure the hydrodynamic radius of the core-shell particles, R_h and the radius of the PMMA particles denoted as R_{core} , assuming that the core of the microgel has radius similar to the radius of PMMA particles synthesized separately.

Figure 3.1 Chemical structure of model (a) pH-responsive cross-linked MAA-EA microgel and (b) MMA core.

(a) Characteristics of cross-linked MAA-EA microgels								
Name of microgel	MAA/EA Molar Ratio (%)	DAP (wt%)	N _x	c ₀ (mole/l)	pH	R _h (α=0) (nm)	Polydispersity Index M _w /M _n	Solid Content (wt%)
HASE-20-80-0	20:80	0.0	0	12.5	2.28	38.2	1.22	9.95
HASE-20-80-0.5	20:80	0.5	507	12.3	1.90	40.1	1.20	9.94
HASE-20-80-0.75	20:80	0.75	338	14.2	1.78	37.5	1.13	10.0
HASE-20-80-1	20:80	1.0	253	16.0	1.84	36.5	1.27	9.91
HASE-20-80-1.5	20:80	1.5	168	15.4	1.75	37.3	1.23	9.92
HASE-20-80-2	20:80	2.0	125	13.7	2.24	39.8	1.25	9.90
HASE-20-80-3	20:80	3.0	82	12.7	1.76	41.7	1.26	10.21
HASE-20-80-4	20:80	4.0	61	13.5	1.80	41.1	1.21	9.88
HASE-30-70-4	30:70	4.0	62	10.0	1.99	45.8	1.30	9.95
HASE-40-60-4	40:60	4.0	63	8.1	1.96	49.3	1.33	9.99
HASE-50-50-4	50:50	4.0	64	6.4	1.85	52.5	1.36	9.96
(b) Characteristics of core-shell microgel								
Name of microgel	MAA/EA Molar Ratio (%)	DAP (wt%)	pH	Weight Ratio core : shell	R _{core} (nm)	R _h (α=0) (nm)	Polydispersity Index M _w /M _n	Solid Content (wt%)
CS-20-80-2	20:80	2.0	1.67	1 : 1.43	84.2	89.5	1.08	11.0
CS-50-50-1	50:50	1.0	1.98	1 : 1.43	84.2	93.5	1.23	10.7

Table 3.1 Characteristic of model pH-responsive (a) cross-linked MAA-EA microgel series and (b) core-shell microgel series.

3.3 PREPARATION OF MICROGEL SAMPLES

The polymer latex at low pH of between 1.8 to 2.5 was dialyzed in distilled deionized water using regenerated cellulose tubular membrane. The dialysis process was carried out over a one-month period where the water was replaced every week. This cleaning process removes all the impurities and unreacted chemicals. The concentration of the stock solutions after dialysis was measured. From the stock solutions, varying concentrations of microgel solutions were prepared for the electromotive measurements, laser light scattering, rheological measurements and turbidimetry experiments.

It is known that in light scattering measurements, stray light and dust are two major problems that have to be eliminated [Joosten et al., 1991]. Brookhaven's cell sample cavity is specially designed to minimize stray light by using the matching liquid in the matching vat (Brookhaven Corporation, 1993). If the laser, index matching vat and the sample cell are properly maintained and aligned, stray light does not pose a significant problem. However, dust is a major problem affecting the results and has to be carefully controlled.

First, the solvent used for light scattering study should be purified. The water used for the solution preparation was obtained from the Millipore Alpha-Q purification system. The system removes ions and other trace organic materials and particles that are larger than 0.45 μm . Second, the sample cells and other glassware should be cleaned very carefully. All the dirty sample cells were soaked in chromic acid to remove any impurities sticking on the wall of the cell. They were then cleaned by

CHAPTER 3 MATERIALS & EXPERIMENTAL TECHNIQUES

using a small brush with soft detergent such as sodium dodecyl sulfate and rinsed thoroughly in tap water followed by several rinses with purified water. Third, filtration and centrifugation were used to remove dust from the samples. Dusts are usually large particles (radius > 1000nm) and they can be driven to the bottom of the test tubes by centrifugation. A BI-SFS sample filtration system was used to remove dust. The samples were pumped through a 0.8 μ m filter at 300 strokes/minute for 20 minutes.

3.4 NEUTRALIZATION OF MICROGEL SAMPLES

The microgel suspensions were neutralized with sodium hydroxide solutions (NaOH). The degree of ionization can be characterized by the degree of neutralization, α , which is the molar ratio of added base to acid groups on the microgels. Upon neutralization, the acid groups become negatively charged resulting in the swelling of the microgels.

The concentration of methacrylic acidic groups, C_p , was determined from the expression:

$$C_p = \frac{10 y c}{86 y + 100 x + 248 z} \quad (3.1)$$

where y , x and z are the targeted molar fractions of MAA, EA and cross-linker DAP respectively as shown in Table 3.1 and c is the concentration of microgels expressed in weight percent. The density of the microgel suspension was checked and found to be very similar to the density of water for all the range of microgel concentration studied here, i.e. $\rho_{\text{polymer solution}} \approx 1 \text{ g/ml}$. Thus, 100g polymer solution $\approx$ 100 ml polymer solution and the slight deviation is within the permissible range for experimental errors.

Potentiometric and conductometric titration experiments have been conducted by Wang [2000] for these cross-linked microgels. The pH and conductivity curves as a function of α exhibited a well-defined equivalence point corresponding to the complete neutralization of MAA groups as confirmed by α of close to 1. Therefore,

the actual molar ratio of MAA and EA in the microgel is very close to the targeted value and the slight deviation is within experimental error of 2 %.

3.5 EQUIPMENT AND EXPERIMENTAL TECHNIQUES

3.5.1 RHEOMETERS AND RHEOLOGICAL MEASUREMENTS

The intrinsic properties of the cross-linked microgels were measured using the Ubbelohde capillary viscometer immersed in the thermostatic bath maintained at a temperature of $25 \pm 0.1^\circ\text{C}$. Since the density, and thus the flow time, depends on temperature, it is necessary to keep the temperature constant. Initially, a certain known volume of solvent was placed in the viscometer to measure the solvent efflux times. The polymer solutions at the concentration of 0.1 wt% was added to the solvent and mixed thoroughly, and then the efflux times of the polymer solutions were measured. The polymer solution in the viscometer was then successively diluted with the solvent and the solution efflux times determined. The efflux times of the solution at different solution concentrations were used to calculate the reduced and inherent viscosities. A standard conductivity meter was used to measure the conductivity of the solution. The conductivity of the solvent must be the same as that of the stock polymer solution in order to maintain a constant polymer-solvent interaction throughout the dilution process.

Careful consideration is required in the choice of solvent and solute concentration. The solution concentration shall be chosen so that the ratio of the efflux time of the

CHAPTER 3

MATERIALS & EXPERIMENTAL TECHNIQUES

solution to the solvent, (t/t_0) is between 1.2 and 2. A lower limit of 1.2 is necessary in order to have sufficient precision on the determination of efflux times. The upper limit of 2.0 is recommended because at high relative molecular mass, there can be shear effects and non-linearity of the concentration in relation to the reduced viscosity.

Rheological studies of semi-dilute to concentrated solutions were carried out using the Carri-Med CSL500 controlled-stress rheometer and Contraves LS40 controlled rate rheometer. Cone and plate with (40mm, 2 degrees), cup and bob geometry were employed to measure high and low viscosity solutions. All the geometry setups were equipped with a water-circulating bath and peltier plate, to ensure a uniform temperature of $25 \pm 0.1^\circ\text{C}$ in the samples. The rheometers were calibrated once a month using silicon calibration oils at three different rotational speeds to verify the accuracy and respond of the rheometers when sensing low, medium and high torques values. Measurements of the same sample were repeated at least twice in order to ensure that the viscosity data were reproducible.

The steady state shear viscosity data presented in this dissertation was conducted under equilibrium viscosity condition. After a steady shearing flow has been imposed on the dispersion for a sufficient period of time, the shear stress approaches a steady state, $\sigma(\dot{\gamma})$, which depends on the imposed shear rate, $\dot{\gamma}$. The ratio of the steady shear stress, σ to the shear rate, $\dot{\gamma}$ is called the steady state shear viscosity or equilibrium viscosity condition. The shear stress reaches a steady value only after a transient period of shearing starting from a state of rest. In order to achieve this condition, sufficient pre-shear time must be allowed to avoid the collection of data in

the transient or start-up flow region. The material was subjected to a constant shear rate experiment and the duration where the material is at its transient state was identified. The total measuring time must be longer than the transient state duration multiplied by the number of measurement points.

3.5.2 ELECTROMOTIVE MEASUREMENTS

The concentration of mobile sodium (Na^+) ions, C_{Na^+} and potassium (K^+) ions, C_{K^+} were determined by electromotive (EMF) measurements using a Na^+ and K^+ ion selective electrodes (Na^+ ISE and K^+ ISE) respectively and an Ag/AgCl electrode as the reference. The titration experiments were conducted using the Radiometer Copenhagen ABU93 Triburette system. Titration of NaCl and KCl solution into water was conducted to calibrate the electrode Na^+ ISE and K^+ ISE respectively. The Nernst equation, which was used to calculate the mobile K^+ ion concentration, C_{K^+} is given as

$$EMF = 241.165 + 49.256 \log C_{\text{K}^+} \quad (3.2)$$

and the mobile Na^+ ion concentration, C_{Na^+} is given as

$$EMF = 241.165 + 49.256 \log C_{\text{Na}^+} \quad (3.3)$$

3.5.3 TURBIDIMETRIC TECHNIQUE

Measurements of transmittance between wavelength of 500 and 900 nm were conducted using a Hewlett Packard UV-Visible Spectroscopy at 25°C. Initial measurements were done using cuvettes with optical path lengths of 0.2, 0.5 and 1 cm to confirm the Beer-Lambert law. Only data with transmissions between 0.03 and 0.95 were found to be accurate enough. In all cases, the turbidity was found to be independent of the length of the optical path within given limits of error of 1 %. From the strict validity of the Beer-Lambert law, it is evident that the determination of τ is not afflicted by multiple scattering or forward scattering. All subsequent measurements were done with cuvettes of 1 cm path length.

3.5.4 LASER LIGHT SCATTERING AND MEASUREMENTS

Static light scattering (SLS) was used to measure and analyze the time-average scattered intensities. The method is often used to determine microscopic properties of particles such as the z-average radius of gyration (R_g), the weight-average molecular weight ($\bar{M}_w$), and the second virial coefficient (A_2) according to Equation (3.4),

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w} \left[1 + \frac{16\pi^2 n^2 \langle R_g^2 \rangle \sin^2\left(\frac{\theta}{2}\right)}{3\lambda^2} \right] + 2A_2 c \quad (3.4)$$

where, the Rayleigh ratio, $R_\theta = (I_s r^2 / I_t \sin \theta)$; $K = [4\pi^2 n^2 (\delta n / \delta c)^2 / (N_A \lambda^4)]$; c is the concentration of the polymer solution; n is the refractive index of the solvent; θ is the angle of measurement; λ is the wavelength of laser light and N_A is the Avogadro's constant. The refractive index increment of the polymer solution, (dn/dc) was measured using a differential refractometer where the values obtained was ~ 0.1 ml/g for all the microgel solutions. A plot of (Kc/R_θ) versus $[\sin^2(\theta/2) + k c]$ (where k is a plotting constant) can be used to determine the molecular parameters. By extrapolating the data to zero angles and concentrations, R_g and A_2 can be obtained from the slopes, respectively. A simultaneous extrapolation to zero angle and concentration yields an intercept, which is the inverse of the $\bar{M}_w$.

Dynamic light scattering (DLS) experiments were performed to determine the microgel particle size. The frequency of scattered light fluctuates around the incident light due to the constant motion of the polymer molecules. Dynamic light scattering (DLS) measures the intensity fluctuations with time and correlates these fluctuations

to the properties of the scattering objects [Chu, 1991; Brown, 1993]. In general, the terms of correlation functions of dynamic variables are always used to describe the response of the scattering molecules to the incident light. From the expression,

$$\Gamma = Dq^2, \quad (3.5)$$

the translational diffusion coefficients, D , can be determined. Γ is the decay rate, which is the inverse of the relaxation time, τ ; q is the scattering vector ($q = (4\pi n \sin(\theta/2))/\lambda$), where θ is the scattering angle, n is the refractive index of the solution, and λ is the wavelength of the incident light. If the Stokes-Einstein equation is used, the apparent hydrodynamic radius, R_h , can be calculated using the following equation:

$$R_h = \frac{kT}{6\pi\eta_s D} \quad (3.6)$$

where k is the Boltzmann constant and η_s is the solvent viscosity.

A Brookhaven BIS200 laser scattering system was used to perform the static and dynamic light scattering experiments. The goniometer system includes focusing optics, a rotating arm, detector optics, photon detector, neutral density filter, beam focus, sample cell assembly, cells, and a high voltage power supply for the detector. The light source is a power adjustable vertically polarized 350 mW argon ion laser with a wavelength of 488 nm. The data obtained from the DLS measurement are the correlation functions represented by either the intensity auto correlation function, $g_2(t)$ or the field autocorrelation function $g_1(t)$. These functions could then be analyzed using the Inverse Laplace Transform technique to obtain the distribution of decay time. The Inverse Laplace Transform analysis method used is REPES supplied with the GENDIST software package and the probability of reject was set to 0.5.

The GENDIST program was used in the analysis of photon correlation spectroscopy (PCS) experiments in the homodyne mode. At the core of this program is the REPES algorithm developed by Jakes at the Institute for Macromolecular Chemistry in Prague. This routine performs an Inverse Laplace Transformation with variable degree of regularization (with a second order regularizer). The fitting was performed directly on $g_2(t)$ rather than $g_1(t)$. Results are presented in graphical form and in tabular form (moments of the distribution). The schematic representation of the system is shown in Figure 3.2.

Figure 3.2 Schematic representation of Brookhaven laser light scattering system [Brookhaven Instrument Corporation, 1993].

The dynamic light scattering (DLS) method is a simple and accurate method to obtain information on the size and polydispersity of the microgels. The field autocorrelation function $g_1(t)$ data can be analyzed using the cumulants method, which is a Non-

Laplace Transform technique introduced by Koppel [Koppel, 1972]. In practice, $\log g_1(t)$ is fitted to a polynomial of second order, which yields the first cumulant, $\bar{\Gamma}$ and the second cumulant, μ_2 . The first cumulant, $\bar{\Gamma}$ is an important quantity, since it can be calculated for many physical systems and situations. The second cumulant, μ_2 is a measure of the width of the distribution $w(\Gamma)$, and hence the effective polydispersity of the sample. For unimodal distributions of moderately polydispersed spherical particles in solution, the second cumulant is given by Eq. (3.7) [Brown, 1993]:

$$\mu_2 / \bar{\Gamma}^2 \approx (M_w / M_n - 1) / 4 \quad (3.7)$$

where M_n is the number averaged molecular weight, M_w the weighted averaged molecular weight. The ratio M_w/M_n is known as the polydispersity index, which gives information on the sample polydispersity, where $M_w/M_n=1$ represents very uniform particle sizes. As the polydispersity of the sample increases, the ratio M_w/M_n becomes greater than 1. The method of cumulants is very sensitive to the distribution of particle sizes, thus providing a quantitative measure of the dispersity of particle sizes in the sample. The information on the polydispersity of the microgels and core-shell particles obtained using Equation (3.7) is included in Table 3.1.

Since the pH-responsive microgels are polyelectrolytes with potentially strong inter-particle interactions, it is necessary to ensure that the concentration of the microgels is sufficiently low such that inter-particle interactions do not affect the light scattering results. The concentration of the microgel solutions used in the light scattering experiments is approximately 0.02 wt%. At low pH, the insoluble polymer yields extremely high scattering intensity, which may damage the detector of light scattering device, hence it is necessary to dilute the polymer solutions. For systems which form

CHAPTER 3

MATERIALS & EXPERIMENTAL TECHNIQUES

precipitates or insoluble particles, neutral density filters of various filtering capacity were placed at the incident laser light to reduce the intensity of the laser beam.

As the equipment is an optical instrument, the laser must be aligned to reduce measurement errors. In addition, the stability of the laser over the measurement period must be routinely checked. The stability test, alignment and adjustment of the equipment are explained in details in the equipment manual (Brookhaven Corporation, 1993). The alignment of the laser optics and detectors were checked by measuring the intensities of toluene between 15 and 155 degrees. The averaged intensity at each of the angle were corrected and compared with that at 90 degrees and the deviations were calculated. Good alignment was obtained when the deviation was less than 2%.

In the DLS measurements, the count rates were controlled by adjusting the pinhole size, and the power of the laser in order to achieve count rates of between 10^5 to 10^6 counts per second. Under such condition, good signal to noise ratio was obtained. The laser was allowed to warm up for at least 30 minutes at the beginning of each day before any experiment was performed. In most experiments, the laser power was adjusted to approximately 100 to 150 mW. Both the SLS and DLS are absolute techniques for determining $\bar{M}_w$ and R_h respectively, and hence they require no additional calibration.

4 MICROSTRUCTURE AND RHEOLOGY OF MAA-EA MICROGELS –EFFECT OF CROSS-LINK DENSITY

As a first step towards developing a generalized approach to model soft microgel particles, it is important to examine a wide variety of model soft sphere systems. In this chapter, the effect of varying microgel cross-linked densities on the swelling behavior and bulk rheological properties of pH-responsive microgels as a function of neutralization degree of the acidic groups will be examined.

4.1 SWELLING AND ELASTICITY

The pH-responsive microgel particles containing 20 mole percent MAA at varying cross-linked densities were characterized in dilute salt free solution using the Brookhaven dynamic light scattering (DLS) system for neutralization degree (α) ranging from 0 to 1. In the unneutralized state, the particles exhibit a microstructure close to that of a model hard sphere with a hydrodynamic radius, R_h of ~ 40 nm. The pH-dependent hydrodynamic radius, R_h , shows a continuous increase as α increases from 0 to 1.0, representing the steady expansion of particles due to enhanced osmotic pressure exerted by the counter-ions trapped inside the polymeric network by the electrostatic attraction exerted from the charged carboxylate groups as depicted in Figure 4.1 and Figure 4.2(a).

Figure 4.1 Schematic representation of microgel particles in the swollen state, cross-linked at different density; (a) low cross-linked density (HASE-20-80-1) and (b) high cross-linked density (HASE-20-80-4). The full dots between chain segments represent the cross-linker. The counter-ions from the base (NaOH) used to neutralize the microgels are represented by the symbol Na⁺ and the symbol ⊖ represents the neutralized carboxylic groups, COO⁻. The outer shell represents the region where electro-neutrality is not satisfied locally.

The swelling characteristics at $\alpha \leq 0.3$ is fairly similar for all the seven microgel systems with 20 mole percent MAA but different cross-linked densities. The R_h begin to deviate from each other when α exceeds 0.3, which suggests a change in conformation of the microgel particles during the neutralization process. The hydrophobic attraction between the EA blocks preserves the existing particle conformation, whereas the osmotic pressure exerted by the counter-ions attracted to the charged carboxylate groups expands the particles to a swollen state. Consequently, a transition region reflecting the conformational change of microgel particles caused by the competition of these two types of interactions is observed.

Figure 4.2 (a) Dependence of hydrodynamic radius, R_h on neutralization degree, α for microgels with 20 mole percent MAA cross-linked at different DAP density (wt% DAP) in salt free solutions; (b) Low shear relative viscosity, η_r as a function of neutralization degree, α of salt free suspension at 5wt% microgel concentration with 20 mole percent MAA cross-linked at different DAP density (wt% DAP).

Below this transition point, the increment in R_h is smaller because the osmotic pressure exerted by the counter-ions is insufficient to overcome the hydrophobic attraction between the EA blocks. As α increases beyond this transition point, the osmotic pressure exceeds the hydrophobic attraction, resulting in a rapid increase in R_h at $\alpha > 0.3$. As anticipated, microgels with lower cross-linked density exhibit larger swelling behavior as observed in Figure 4.1 and 4.2(b). The maximum R_h for HASE-20-80-0.5 is ~ 180.0 nm, compared to ~ 87.8 nm for HASE-20-80-4.

Figure 4.2(b) depicts the low-shear relative viscosity, $\eta_r(\eta_0/\eta_s)$ versus the degree of neutralization, α for salt free solution containing 5 wt% microgel with 20 mole percent MAA and different cross-linked densities. At $\alpha = 0$, where the colloidal particles are in

the form of a compact sphere, the viscosities for all microgel systems are nearly identical to the viscosity of water (i.e. solvent), where $\eta_r \sim 1$. The viscosity increases continuously as α increases from 0 to 1.0, and microgel HASE-20-80-1 exhibits the largest viscosity increase.

Similar trend is observed where the viscosity begins to increase at a faster rate as reflected by the sharp increase in η_r at $\alpha > 0.3$, which further points to a transition region reflecting the conformational change of microgel particles during the neutralization process, as discussed earlier. At lower cross-linked density, the particles exhibit significantly larger swelling, which reduces the inter-particle distance. Hence, for a fixed amount of neutralized carboxylate groups (or same neutralization degree), stronger inter-particle interaction is observed with HASE-20-80-1 compared to HASE-20-80-4.

4.2 STEADY SHEAR VISCOSITY DEPENDENCE ON DEGREE OF NEUTRALIZATION AND MICROGEL CONCENTRATION

Figures 4.3(a) to 4.3(d) display the flow properties of 5 wt% microgel particles with different DAP densities at different neutralization degrees. [Note: Only four sets of data are shown here, and the remaining data are not included due to over crowding of data. They are however shown in Figure 4.4 (b)]. As shown in Figures 4.3(a) and 4.3(d), HASE-20-80-0.5 and HASE-20-80-4 exhibit predominantly Newtonian behavior at shear rates of less than 50 s^{-1} . The shear viscosity is independent of shear rates at low α , and the viscosity increases progressively with degree of neutralization.

Figure 4.3(b) demonstrates that HASE-20-80-1 shows significant shear-thinning behavior at $\alpha > 0.5$. At low α (< 0.5), the sample displays a Newtonian behavior with viscosity nearly identical to the viscosity of water (i.e. solvent), where $\eta_r \sim 1$. The effective volume, ϕ_{eff} of the microgel particles in solution is small due to low degree of swelling because only up to 50 % of the carboxylic acids are neutralized to carboxylate groups. At $\alpha > 0.5$, the enhanced osmotic pressure exerted by the counter-ions trapped inside the polymeric network by the large number of charged carboxylate groups causes the MAA-EA particles to swell further, resulting in an increase in the effective volume, ϕ_{eff} occupied by the particles. Such increase essentially decreases the inter-particle distance, where the interaction forces between the swollen particles increase sharply, resulting in the shear-thinning behavior. The dependence of the viscosity on shear rate occurs when the imposed deformation perturbs the inter-particle interaction forces. At large deformation, the hydrodynamic contribution to the shear stress dominates and the

Brownian contribution becomes insignificant. The low shear rate viscosity plateau, η_0 was determined from a regression fit to the Cross model,

$$\frac{\eta}{\eta_0} = \frac{1}{1 + (\kappa \dot{\gamma})^m} \quad (4.1)$$

which is known to provide a good description of the viscosity of colloidal suspension [Cross, 1965]. The model fittings to Equation (4.1) are represented by the solid lines in Figures 4.3 and a table of the Cross model parameters is given in Appendix B.

Figure 4.3 Relative viscosity, η_r versus shear rate of salt free microgel suspension at 5wt% polymer concentration with 20 mole percent MAA at four different degree of neutralization, α ($\bigcirc$:0 ; $\diamond$:0.5 ; $\square$:0.8 ; $\triangle$:1.0) and four different cross-linked density (wt% DAP): (a) 0.5 wt%; (b) 1.0 wt%; (c) 2.0 wt%; and (d) 4.0 wt%. The solid lines represents fittings according to Equation (4.1).

4.3 OPTIMUM CROSS-LINKED DENSITY

4.3.1 RHEOLOGICAL ANALYSIS

When the relative viscosity of cross-linked MAA-EA microgel is plotted as a function of cross-linked density (wt%) for each neutralization degree, α and microgel concentration, c (wt%) as illustrated in Figures 4.4(a) and 4.4(b), it is observed that the general trend of the viscosity profiles is identical in both varying α and c (wt%). The viscosity increases sharply with cross-linked density, reaching a maximum at 1 wt% DAP, where it decreases with increasing DAP content up to 4 wt%. The relative viscosity can change by more than three orders of magnitude, for example, 5 wt% MAA-EA microgel at $\alpha = 1$ possesses a η_r of ~ 7 at 0 wt% DAP and it increases to ~ 13000 at 1 wt% DAP.

Figure 4.4 Relative viscosity, η_r as a function of cross-linked density (wt% DAP) of microgel with 20 mole percent MAA at; (a) polymer concentration of 5 wt% with different neutralization degree, α and; (b) different polymer concentration, c (wt%) of the fully neutralized microgel ($\alpha = 1$).

4.3.2 MOLECULAR WEIGHT ANALYSIS

In order to fully understand the trend shown in Figure 4.4, static light scattering experiments were conducted to determine the molecular weight, M_w and second virial coefficient, A_2 of the microgels at different cross-linked densities for α of 0 and 1 respectively. The Zimm plot (described by Equation (3.4)) of HASE-20-80-2 is shown in Figure 4.5 at $\alpha = 0$ (Figure 4.5(a)) and $\alpha = 1$ (Figure 4.5(b)).

Figure 4.5 Zimm plot of HASE-20-80-2 at (a) $\alpha = 0$ and (b) $\alpha = 1$ in aqueous solution at room temperature where the polymer concentration range was from 0.001 to 0.01 mg/ml.

Results from static light scattering (Figures 4.6(a) and 4.6(b)) show clearly that before neutralization ($\alpha = 0$), the microgel particles possess a molecular weight of between 180 to 200×10^6 g/mol and a negative second virial coefficient of $\sim -1.0 \times 10^{-4}$ cm³mol/g² regardless of cross-linked densities. This is due to the seeded emulsion polymerization process employed where an in-situ seed product with approximately similar number of monomer units (hence similar M_w) were cross-linked together to produce a compact

particle consisting of several polymer chains. A negative A_2 suggests that the particle-solvent interaction is poor because of the carboxylic acid and ethyl acrylate segments, which formed a compact insoluble spherical particle.

However, when the carboxylic acid groups are fully neutralized (at $\alpha = 1.0$), the M_w of the uncross-linked copolymer decreases to $\sim 2 \times 10^6$ g/mol with a positive A_2 of ~ 0.01 cm³mol/g². As cross-linked density increases, molecular weight of the fully neutralized copolymer increases up to an asymptotic value of $\sim 200 \times 10^6$ g/mol and the A_2 values remain positive but decreases to $\sim 3.8 \times 10^{-4}$ cm³mol/g² at 1 wt% DAP. Beyond 1 wt% DAP, M_w remains almost unchanged with only a slight decrease in A_2 to $\sim 2.0 \times 10^{-4}$ cm³mol/g² at 4 wt% DAP.

Figure 4.6 Results from static light scattering illustrating the dependence of (a) molecular weight, M_w and (b) second virial coefficient, A_2 on cross-linked density (wt% DAP) of microgel with 20 mole percent MAA both at the unneutralized ($\alpha = 0$) and fully neutralized state ($\alpha = 1$).

Figures 4.4 and 4.6 clearly indicate that HASE-20-80 microgels exhibit a maximum viscosity at cross-linked density of 1 wt% DAP. Further static light scattering experiments were conducted on two microgels, one below the optimal cross-linked density (i.e HASE-20-80-0.5) and another above the optimal cross linked density (i.e HASE-20-80-2). Figures 4.7(a) and 4.7(b) compare the molecular weight, M_w and the second virial coefficient, A_2 of the two microgels as a function of neutralization degree, α . The M_w of HASE-20-80-0.5 microgel decreases progressively from $\sim 200 \times 10^6$ g/mol to $\sim 50 \times 10^6$ g/mol while the A_2 increases progressively as α increases to 1. On the other hand, the M_w of HASE-20-80-2 microgel remains almost unchanged with only a slight increase in the A_2 value as α increases to 1.

Figure 4.7 Results from static light scattering illustrating the dependence of (a) molecular weight, M_w and (b) second virial coefficient, A_2 , on neutralization degree, α of HASE-20-80-0.5 and HASE-20-80-2.

4.3.3 THEORETICAL SCALING ANALYSIS

To further rationalize the observed optimum cross-linked density, the approach proposed by Cloitre and co-workers [Cloitre et al., 2003] was used, where the variations of the relative swelling of the microgels with the cross-linked density, N_x and the degree of neutralization, α were determined and checked against the theoretical scaling law given by Equation (2.19),

$$Q \propto (\alpha N_x)^{3/2}.$$

Figure 4.8(a) shows that the swelling ratio at maximum swelling ratio Q_m ($\alpha=1$) is proportional to $N_x^{3/2}$ for N_x less than ~ 252 which corresponds to cross-linked density greater than 1 wt% (represented by the solid line).

When N_x is larger than 252 (i.e. cross-linked density of 0.75 wt% and 0.5 wt% DAP), the proportionality is no longer valid, and the maximum swelling Q_m is significantly lower than that predicted by the scaling relationship.

Similarly, the variations of normalized swelling ratio, Q/Q_m as a function of $\alpha^{3/2}$ as shown in Figure 4.8(b) also suggest a discontinuous volume transition at $\alpha \leq 0.3$. Above the volume transition ($\alpha > 0.3$), the data measured for cross-linked densities ranging from 1 to 4wt% DAP fall on a single master curve (represented by the solid line) which agrees with the theoretical prediction, whereas data for 0.5 and 0.75 wt% DAP deviated from the master curve.

Figure 4.8 (a) Variations of the maximum swelling ratio, Q_m at $\alpha=1$ as a function of cross-linked density, $N_x^{3/2}$. Solid line represents the region where Equation (2.19) is valid; (b) Variations of the normalized swelling ratio Q/Q_m as a function of α , for microgel with 20 mole percent MAA at different cross-linked densities (wt% DAP) (● :0.5 ; □ : 0.75 ; ▲ :1.0 ; ○ :1.5 ; ■ : 2.0 ; △ :3.0 ; ◆ :4.0). The master curve is represented by the solid line.

The deviation clearly suggests that at cross-linked density lower than 1 wt% DAP, there are insufficient cross-linked junctions to produce a stable microgel particle. In addition to particle swelling, there is substantial expulsion of polymer chains from the particles during neutralization, which causes the maximum swelling ratio Q_m to be lower than the theoretical prediction due to the loss of polymer chains and the deswelling effects.

Figure 4.9 shows that the variations of swelling ratio, Q as a function of $(\alpha N_x)^{3/2}$ for microgels with varying cross-linked densities and neutralization degree, fall on a master curve, and this confirmed that Q is proportional to $(\alpha N_x)^{3/2}$. However, two master curves with different proportionality constants (represented by the slope of the line) are

observed at $\alpha \leq 0.3$ (below the volume transition) and $\alpha \geq 0.4$ (beyond the volume transition). It is believed that the discontinuous volume transition at $\alpha \leq 0.3$ reflects the conformational change of microgel particles and the different degree of swelling during the neutralization process due to the competition between the hydrophobic attraction between the EA blocks and the osmotic pressure exerted by the counter-ions attracted to the charged carboxylate groups, as discussed earlier.

Figure 4.9 Variations of the swelling ratio, Q as a function of $(\alpha N_x)^{3/2}$ for microgels with varying cross-linked densities, N_x and neutralization degree, α . The solid line and the dotted line represents the master curve for the data at $\alpha \geq 0.4$ and $\alpha \leq 0.3$ respectively.

Figure 4.10 illustrates the conformational transition of the cross-linked microgel with 20 mole percent MAA as a function of cross-linked density by comparing the molecular weight and relative viscosity at 5 wt% microgel concentration. Below the optimum level of 1 wt% DAP, there are insufficient cross-linked junctions to produce a stable and compact microgel particle. The reduction in the molecular weight, M_w upon neutralization confirmed that in addition to particle swelling, there is substantial expulsion of polymer chains from the microgel particles. The large increase in A_2 upon neutralization suggests that the polymer-solvent interaction is enhanced due to exposure of negatively charged carboxylate groups to the solvent environment when the particle swells and the chains expelled from the swollen particles.

As cross-linked density increases, M_w increases and approaches an asymptotic value at a critical cross-linked density of 1 wt% DAP, where the M_w of unneutralized and neutralized particle are identical. The critical point of 1 wt% DAP is the optimum cross-linked density for microgel with 20 mole percent MAA to yield an optimal swollen microgel particle. The reduction in the second virial coefficient indicates that the interaction between charged carboxylate groups and solvent is suppressed by the constraints of cross-linked junctions. The state of the microstructure controls the rheological property, such as viscosity, for e.g. a maximum relative viscosity of 13,000 was observed at the optimum DAP density of 1 wt%. With increasing cross-linked density, the swelling of microgel particles is inhibited, resulting in a larger inter-particle distance and a lower effective volume fraction and a corresponding reduction in the relative viscosity.

Figure 4.10 Illustration of the conformational transition for the cross-linked microgel particle with 20 mole percent MAA as function of cross-linked density (wt% DAP). The filled circle represents M_w and the open circle represents the low shear relative viscosity at 5 wt% polymer concentration.

4.4 SUMMARY

The most striking feature observed is that copolymer with 20 mole percent MAA possesses an optimum cross-linked density of 1 wt% DAP, independent of neutralization degree, α and polymer concentration c . Below the critical level of 1 wt% DAP, insufficient cross-linked junctions are present to form permanent junctions to produce a stable microgel particle. Beyond 1 wt% DAP, the polymer particles are sufficiently cross-linked, which give rise to stable microgel particles, whose size decreases with increasing cross-linked density. Comparison with the theoretical scaling law given by Equation (2.19) indicates that the swelling ratio at maximum swelling Q_m ($\alpha = 1$) does not scale with $N_x^{3/2}$ for cross-linked density lower than 1 wt%. This confirmed that there is substantial expulsion of polymer chains from the particles during neutralization, which causes the maximum swelling ratio Q_m to be lower than theoretical prediction. By combining the results from light scattering and rheological measurements, we are able to correlate the microstructural evolution of microgel systems to their bulk rheological behavior.

5 MICROSTRUCTURE AND RHEOLOGY OF MAA-EA MICROGELS –EFFECT OF MAA CONTENT

The second series of model soft microgel particles that we hope to gain new insights consists of cross-linked pH-responsive microgels with varying molar ratio of acidic groups (MAA). In this chapter, we performed quantitative studies to investigate the swelling behavior (microscopic) and rheological (macroscopic) properties of this model microgels with varying MAA groups as a function of neutralization degree.

5.1 SWELLING AND ELASTICITY

5.1.1 PARTICLE SIZE CHARACTERIZATION

The pH responsive MAA-EA microgel particles with fixed cross-linked density but varying MAA/EA molar ratio were characterized in dilute salt free solution by DLS for α ranging from 0 to 1.0. The relative change of the hydrodynamic radius, R_h , as a function of α for MAA-EA microgel cross-linked with 4wt% DAP i.e. (HASE20-80-4), (HASE-30-70-4), (HASE-40-60-4) and (HASE-50-50-4) is shown in Figure 5.1(a). The pH-dependent hydrodynamic radius shows a gradual increase as α increases from 0 to 1, representing the steady expansion of particles due to enhanced osmotic pressure exerted by the counter-ions trapped inside the polymeric network by the electrostatic attraction exerted from the charged carboxylate groups. As anticipated, the microgels with a lower MAA-EA molar ratio are less swellable.

As observed from Figure 5.1(a), at $\alpha = 0$ (before neutralization), R_h for the microgel with larger proportion of MAA content is larger. For example, R_h is 40 and 50 nm for MAA/EA molar ratio of 20/80 and 50/50 respectively. This observation may be explained as follows. During the seeded emulsion polymerization, more EA will tend to reside in the core of the particle, as it is more hydrophobic. MAA on the other hand is more hydrophilic and hence is more compatible with water. Thus, more MAA will tend to remain on the surface of the particle and the particle size will be larger as the amount of MAA increases during polymerization.

Figure 5.1 (a) Dependence of hydrodynamic radius, R_h on neutralization degree, α for microgels cross-linked with 4 wt% DAP at different MAA/EA molar ratio in salt free solutions; (b) Low shear relative viscosity, η_r as a function of neutralization degree, α of salt free suspension at 5 wt% microgel concentration with different MAA/EA molar ratio.

Figure 5.1(b) shows a plot of the relative zero-shear viscosity of microgel at different MAA/EA molar ratio versus the degree of neutralization, α . Microgels with higher MAA content possesses a larger effective volume fraction at a particular α , thus enhancing the interaction between colloidal particles, which is reflected in the higher relative viscosity.

It is evident from Figures 5.1(a) and (b) that similar trend is observed where the particle size and viscosity begins to increase at a faster rate as reflected by the sharp increase at $\alpha > 0.3$, which further points to a transition region reflecting the conformational change of microgel particles during the neutralization process, as discussed earlier. Potentiometric titrations were conducted by Wang on the cross-linked MAA-EA microgels with different MAA/EA molar ratios [Wang, 2000]. An apparent plateau or transition region was detected in the titration curves, which suggests that a change in conformation of microgel particles caused by the competition of hydrophobic attraction and Coulombic repulsion was encountered in the neutralization process as explained in Section 4.1.

5.1.2 THEORETICAL SCALING ANALYSIS

The theoretical scaling law, $Q \propto (\alpha N_x)^{3/2}$ was derived for microgels with fixed molar fraction of acidic units, y . We extended the above scaling law to include new data containing varying amounts of MAA in the microgel system, with y of 0.2, 0.3, 0.4 and 0.5. We tested the expanded scaling law $Q \propto (y\alpha N_x)^{3/2}$ as shown in Figure 5.2 where all the data at $\alpha \geq 0.4$ fall on a master curve, and this confirmed that Q is proportional to $(y\alpha N_x)^{3/2}$ for microgels with varying cross-linked densities, molar fraction of acidic units and neutralization degree.

When regression analysis was performed on the experimental data, at $\alpha \leq 0.3$ (below the volume transition) and $\alpha \geq 0.4$ (beyond the volume transition) (represented by the dotted and solid lines respectively), we observed two proportionality constants. The constant (represented by the slope of the fitted equation) is lower at $\alpha \leq 0.3$ (~ 0.143) compared to $\alpha \geq 0.4$ (~ 0.183). This difference in the degree of swelling during the neutralization process is due to the competition between the hydrophobic attraction between the EA blocks and the osmotic pressure exerted by the counter-ions attracted to the charged carboxylate groups, as discussed earlier.

Figure 5.2 Variations of the swelling ratio, Q as a function of $(y \alpha N_x)^{3/2}$ for microgels with varying cross-linked densities, N_x , molar fraction of MAA units, y and neutralization degree, α . The solid line and the dotted line (see inset graph) represents the fitted line when the data was curve fitted at $\alpha \geq 0.4$ and $\alpha \leq 0.3$ respectively. The linear equations of the fitted lines are shown in the figure.

5.2 STEADY SHEAR VISCOSITY DEPENDENCE ON DEGREE OF NEUTRALIZATION

Figures 5.3(a) and 5.3(b) display the flow behaviors at a higher concentration of 5 wt% for HASE-20-80-4 and HASE-30-70-4 while Figures 5.3(c) and 5.3(d) are for 4 wt% microgel concentration of HASE-40-60-4 and HASE-50-50-4.

Figure 5.3 Shear viscosity, η versus shear rate, $\dot{\gamma}$ at five different degree of neutralization, α ($\bigcirc$:0 ; $\blacktriangle$:0.2 ; $\diamond$:0.5 ; $\square$:0.8 ; $\triangle$:1.0) of HASE cross-linked with 4 wt% DAP with different MAA/EA molar ratio : (a) 20/80; (b) 30/70; (c) 40/60; and (d) 50/50.

HASE-20-80-4 shows Newtonian behavior for the complete range of degree of neutralization. On the other hand, the flow behavior for HASE-30-70-4, HASE-40-60-4 and HASE-50-50-4 exhibit shear-thinning characteristics at $\alpha = 0.6, 0.5$ and 0.3 respectively. To describe further the severity of shear-thinning, the Cross model (Equation (4.1)) and the Power Law model $\eta = K_2 \dot{\gamma}^{n-1}$ was used to determine the critical shear rate, $\dot{\gamma}_s$ and power law index, n as a function of degree of neutralization, α . The model fittings are represented by the solid lines in Figures 5.3 and the values of $\dot{\gamma}_s$ and n are shown in Figures 5.4(a) and (b).

Figure 5.4 (a) Shear rate for the onset of shear-thinning, $\dot{\gamma}_s$ and (b) Power law index, n for the shear thinning region as a function of neutralization degree, α , for microgels cross-linked with 4 wt% DAP at different MAA/EA molar ratio; ($\blacklozenge$) 20/80; ($\circ$) 30/70; ($\blacksquare$) 40/60; and ($\triangle$) 50/50.

It is observed that the general trend of n and $\dot{\gamma}_s$ is similar for varying α s. The shear rate $\dot{\gamma}_s$ and n decreases with increasing neutralization degree and MAA/EA ratio but the reduction in $\dot{\gamma}_s$ and n as a function of α becomes larger as MAA/EA ratio increases from 20 to 50 mole %. At complete neutralization, $\alpha=1.0$, $\dot{\gamma}_s$ decreases by more than seven orders of magnitude, where it is $\sim 52 \text{ s}^{-1}$ for 20 mole % MAA and reduces to $\sim 1 \times 10^{-6} \text{ s}^{-1}$ at 50 mole % MAA. The rate of shear thinning represented by the power-law index, n increases ~ 6.5 times when MAA/EA molar ratio increases from 20 to 50 mole %. At a fixed value of $\dot{\gamma}_s$ for example $\dot{\gamma}_s = 1.0 \text{ s}^{-1}$, we observed that the neutralization degree required for the viscosity of HASE-50-50, HASE-40-60 and HASE-30-70 to shear-thin are $\alpha = 0.45, 0.60$ and 0.85 respectively.

In order to perturb particle interaction forces and cause shear-thinning at the same shear rate, $\dot{\gamma}_s$ of 1.0 s^{-1} , HASE-30-70-4 at 5 wt% microgel concentration requires $\sim 85\%$ neutralized carboxylic groups to generate the necessary particle-particle interaction that respond to the applied shear deformation. However, the 4 wt% HASE-40-60-4 and HASE-50-50-4 requires at least ~ 60 and $\sim 45 \%$ of its neutralized carboxylic groups to generate similar effects. It is observed that the general trends of n and $\dot{\gamma}_s$ is similar for varying α . The shear rate $\dot{\gamma}_s$ and n reduces with the increase in neutralization degree and MAA/EA ratio.

5.3 DYNAMIC VISCOELASTICITY

The curve for HASE-40-60-4 and HASE-50-50-4 at 4 wt% shown in Figure 5.3(c) and (d) suggests that for $\alpha > 0.8$, the flow is very shear-thinning even at shear rate as low as 10^{-5} s^{-1} . No zero-shear-viscosity plateau is evident. Instead, at high microgel concentrations and high MAA content, the swollen MAA-EA microgel possesses strong electrostatic repulsion that imparts significant viscoelasticity, thus the elastic moduli can be measured.

An amplitude sweep experiment at a fixed frequency was performed to determine a suitable amplitude value, where the material exhibits the linear viscoelastic behavior. This amplitude value was later used in the frequency sweep experiments to determine the frequency dependence of storage and loss modulus, G' and G'' respectively. This procedure ensures that the dynamic property measurements were carried out in the linear viscoelastic region. Figures 5.5(a) and (b) show the storage and loss modulus, G' and G'' as a function of frequency, ω of HASE-40-60-4 microgel at different microgel concentrations, c (wt%) and different neutralization degree, α respectively.

At low microgel concentrations ($c < 3\text{wt}\%$) and low neutralization degree ($\alpha < 0.5$), the samples behave as viscoelastic liquid with $G' < G''$ and the loss modulus approaches the asymptotic behavior of $G'' \propto \omega$. Increasing microgel concentrations ($c > 3\text{wt}\%$) and neutralization degree ($\alpha > 0.5$), the samples change to a viscoelastic solid and the storage modulus is larger than the loss modulus over the whole frequency range. G' is independent of frequency and corresponds to the plateau modulus, G_p .

Figure 5.5 Storage and loss modulus, G' and G'' as a function of frequency, ω of HASE-40-60-4 microgel at different conditions; (a) varying microgel concentrations, c (wt%) (2, 3, 4 and 5wt%) and (b) varying neutralization degree, α (0.2, 0.5, 0.8 and 1.0).

The plateau modulus G_p increases with c and α and a master-curve (represented by the solid line) was obtained when G_p was plotted against ϕ_{eff} as depicted in Figure 5.6. The effective volume fraction of soft microgel particles at various particle concentrations was determined using the proposed semi-empirical approach, which will be explained in detailed in Chapter 7. The term specific volume, k of microgels was introduced where k was determined from the mathematical fitting of the data to the form of the modified Krieger-Dougherty equation shown in Equation (2.22). The effective volume fraction of microgels, ϕ_{eff} was then calculated from $\phi_{\text{eff}} = k c$.

Based on Figures 5.6, the plateau modulus G_p is a strong function of the effective volume fraction and the effect of pH-dependent swelling on the modulus is minimized when ϕ_{eff} was used as the concentration variable. Wagner pointed out that the elastic plateau modulus, G_p can be related to the interaction potential and the pair correlation function of microgel particles [Wagner, 1993; Bergenholtz et al., 1998]. It is interesting to note that the master curve in Figure 5.6 almost resembles the form of the Krieger- Dougherty (K-D) model (Equation (2.3)), where G_p (which is also a function of the particles interaction potential) increases exponentially at maximum volume fraction, $\phi_m \sim 0.63$. This is another evidence that the generalized approach (details will be given in Chapter 7) is able to capture the physics of soft microgel particles. From Figures 5.5(a) and (b), we observed two distinct regions of viscoelasticity, where the particles behave as viscoelastic liquid, $G' < G$ at $\phi_{\text{eff}} < 0.55$ and viscoelastic solid, $G' > G$ at $\phi_{\text{eff}} > 0.55$.

Figure 5.6 Plateau modulus, G_p as a function of effective volume fraction, ϕ_{eff} at different neutralization degree, α . The solid line represents the master-curve and the dotted line is to illustrate the two different regions of viscoelasticity.

5.4 SUMMARY

The pH-dependent hydrodynamic radius, R_h and viscosity of this microgel systems increase when the molar ratio of MAA groups increases. The theoretical scaling law, $Q \propto (\alpha N_x)^{3/2}$ was successfully expanded to include new data containing varying amounts of MAA, y in the microgel system. Excellent agreement was obtained where all the data fall on a master curve, and this confirmed that Q is proportional to $(y \alpha N_x)^{3/2}$ for microgels with varying cross-linked densities, molar fraction of acidic units and neutralization degree as predicted.

At high microgel concentrations and high MAA content, the swollen MAA-EA microgel possesses strong electrostatic repulsion that imparts significant viscoelasticity. The plateau modulus G_p increases with concentration and α and a master-curve was obtained when G_p was plotted against ϕ_{eff} . This is clear evidence that G_p is a function of the effective volume fraction and the effect of pH-dependent swelling on the modulus is minimized when the ϕ_{eff} is used as the concentration variable.

6 MICROSTRUCTURE AND RHEOLOGY OF MAA- EA MICROGELS –EFFECT OF IONIC STRENGTH

It has been reported that the particle size of soft polyelectrolyte microgel particles could be manipulated by changing the solvent conditions and ionic strength. It is believed that such changes do have a significant impact on their bulk rheological property. This chapter examines the effect of ionic strength on the swelling behavior and rheological properties of pH-responsive polyelectrolyte microgels, where the salt concentration in the bulk solution of the microgel suspension was varied.

6.1 PARTICLE SIZE CHARACTERIZATION

The pH-responsive microgel particles with varying MAA content and cross-linked densities were characterized in dilute solution using dynamic light scattering (DLS) system for neutralization degree (α) ranging from 0 to 1 and in salt concentration ranging from 0.1 to 100 mM KCl.

Figure 6.1 Results from dynamic light scattering illustrating the dependence of R_h on α for (a) HASE-20-80-2 at different salt concentrations, [KCl] and (b) HASE-20-80 with different cross-linked density at salt concentration of 100 mM KCl.

In the unneutralized state, the particles exhibit a microstructure close to that of hard sphere with a hydrodynamic radius, R_h of ~ 35 nm. Swelling is reduced when salt concentration increases as depicted in Figure 6.1(a) for HASE-20-80-2 at varying α . When [KCl] increases from 0.1 to 100 mM, R_h decreases from ~ 108 to ~ 72 nm, which is attributed to the charge shielding effect of the counter ions (salt) on the negatively charged carboxylate groups, thus reducing the osmotic pressure inside the microgels. The swelling behavior of microgels with 20 mole percent MAA in salt concentration of 100 mM KCl (Figure 6.1(b)) is identical to microgels in salt free solutions (Figure 4.1(a)) where a similar transition region reflecting the conformational change of particles during the neutralization process is observed.

6.2 EFFECT OF IONIC STRENGTH ON MOBILE COUNTER-IONS

In the presence of salt, there are two types of counter-ions present i.e. K^+ from the added salt KCl and Na^+ from NaOH to neutralize the microgels. It was observed in Section 6.1.1 that particle size decreases when salt is added due to the charge shielding effect of salt, which reduces the osmotic pressure inside the microgels. Based on this physical insight, the assumption that all the counter-ions associated with ionised units are trapped inside the polymeric network is no longer valid, as it is for the case of salt free solutions.

We postulate that not all the counter-ion from salt, K^+ remain mobile in the solvent environment but a portion of these ions can penetrate the porous microgel particles to shield the negatively charged carboxylate groups. A consequence of this is that some of the Na^+ counter-ions that are inside the particles are expelled, thereby regaining their translational entropy and become mobile sodium ions in the bulk solution. This hypothesis can be confirmed by measuring the concentrations of mobile K^+ ions, C_{K^+} and mobile Na^+ ions, C_{Na^+} in the bulk solution at varying α and different salt concentrations, [KCl].

An accurate method to determine C_{K^+} and C_{Na^+} is to measure the concentration of mobile K^+ and Na^+ ions as a function of neutralization degree using the potassium (K^+) and sodium (Na^+) ion selective electrode (ISE) respectively. Figure 6.2(a)

displays the concentrations of mobile K^+ ions calculated using the Nernst equation, (Equation (3.2)),

$$EMF = 241.165 + 49.256 \log C_{K^+}$$

and Figure 6.2(b) displays the concentrations of mobile Na^+ ions calculated using Equation (3.2)),

$$EMF = 241.165 + 49.256 \log C_{Na^+}.$$

for HASE-20-80-2 at varying α and four different salt concentrations, [KCl].

Figure 6.2 Concentration of mobile counter-ions (a) potassium, C_{K^+} and (b) sodium, C_{Na^+} , calculated using the Nernst equation, Equation (3.2) and (3.3) for HASE-20-80-2 at varying α and four different salt concentrations, [KCl].

Figure 6.2(a) shows that the mobile K^+ ions in the bulk solution undergoes a slight decrease in concentration with increasing α and the change in C_{K^+} is less significant when the salt concentration is high. On the other hand, the mobile Na^+ ions in the

bulk, C_{Na^+} increases with α and becomes more significant at higher salt concentration (Figure 6.2(b)). The slight decreases in C_{K^+} with increasing α confirms the hypothesis that a small portion of mobile K^+ ions in the bulk can penetrate the porous microgel particles and shield the negatively charged carboxylate groups. Consequently, some of the Na^+ counter-ions inside the particles are expelled, which is confirmed by the increase in the mobile Na^+ ions in the bulk solution. As the salt concentration increases, charge shielding effects becomes more significant, resulting in a higher expulsion of Na^+ counter-ions from the swollen particles, which reduces the osmotic pressure inside the microgels and a higher C_{Na^+} was detected in the bulk. Figures 6.3(a) and (b) illustrate the effect of salt (K^+) on the counter-ions inside the microgels and in the bulk solution at low salt and high salt environment respectively.

Figure 6.3 A pictorial representation of the effect of salt (K^+) on the counter-ions (Na^+) inside the microgels and in the bulk solution at different salt concentration regimes; (a) low salt; and (b) high salt environment.

6.3 THEORETICAL SCALING ANALYSIS

The theoretical scaling law, $Q \propto (y\alpha N_x)^{3/2}$ was derived for microgel systems with no added salt, which assumes that all the counter-ions associated with ionised units are trapped inside the polymeric network by the electrostatic attraction exerted by the fixed charges. The above scaling law is extended to include new data containing microgel systems with varying salt concentrations [KCl] and the derivation of this new scaling law is discussed in this section.

As discussed in Section 2.5.2, the equation for the swelling of microgels is determined by the balance between the osmotic pressure inside the microgels and the osmotic pressure outside, as described by Equation (2.16) [Cloitre et al., 2003];

$$\Pi_{in} + \Pi_{el} = \Pi_{out}.$$

Π_{el} is the elastic pressure of the polymeric network described by Equation (2.17);

$$\Pi_{el} = -\frac{RTc_0}{2N_x Q^{1/3}}$$

where $Q = (R_\alpha / R_{\alpha=0})^3$ is the swelling ratio of microgels, N_x the cross-linked density and c_0 the polymer concentration in the particles at collapsed state. The terms Π_{in} and Π_{out} can be described by Equation (2.18);

$$\Pi_{in(out)} = RT C_{in(out)},$$

where C_{in} and C_{out} are the concentrations of the ions inside and outside the microgels.

In the presence of salt and when equilibrium is achieved, C_{out} corresponds to the measured concentration of salt ions in the bulk solution given as,

$$C_{\text{out}} = C_{\text{K}^+} . \quad (6.1)$$

In the absence of salt, all the counter-ions associated with the ionized units are trapped inside the polymeric network by the electrostatic attraction exerted by the fixed charges, $C_{\text{in}} = \alpha c_0 y / Q$. However, when salt is added to the colloidal solution, some of the Na^+ ions inside the particles are expelled to the bulk solution is C_{Na^+} as confirmed experimentally in Figures 6.2(b) and 6.3(b). Hence, the concentration of counter-ions inside the microgels decreases and is described by the expression below,

$$C_{\text{in}} = \alpha c_0 y / Q - C_{\text{Na}^+} . \quad (6.2)$$

By combining Equations (2.16) to (2.18) and Equations (6.1) and (6.2), the swelling ratio Q of the microgels as a function of neutralization degree, α , cross-linked density, N_x , molar fraction of acidic units, y and concentration of mobile counter-ions, C_{K^+} and C_{Na^+} can be obtained, and is represented by Equation (6.3),

$$\left(\frac{\alpha y c_0}{Q} - C_{\text{Na}^+} \right) - \frac{c_0}{2 N_x Q^{1/3}} = C_{\text{K}^+} \quad (6.3)$$

which no longer assumes that all the counter-ions are trapped inside the microgels. Rearranging Equation (6.3), we obtained a new scaling law that takes into consideration the salt concentration and mobile counter-ions,

$$\frac{N_x}{c_0} (C_{\text{K}^+} + C_{\text{Na}^+}) Q + Q^{2/3} \propto y N_x \alpha \quad (6.4)$$

which reduces to $Q \propto (y \alpha N_x)^{3/2}$ when no salt is added, i.e., $C_{\text{K}^+} + C_{\text{Na}^+} \approx 0$.

The new scaling law (Equation (6.4)) was tested as shown in Figures 6.4 where all the data at $\alpha \geq 0.4$ fall on a master curve, and confirmed that

$\frac{N_x}{c_0} (C_{K^+} + C_{Na^+}) Q + Q^{2/3}$ is proportional to $y N_x \alpha$ for microgels with varying

cross-linked densities, molar fraction of acidic units, neutralization degree and salt concentrations. Similarly, two regions with different proportionality constants are observed at $\alpha \leq 0.3$ and $\alpha \geq 0.4$, which represents the difference in the degree of swelling during the neutralization process due to the competition between the hydrophobic attraction between the EA blocks and the osmotic pressure exerted by the counter-ions, as discussed earlier.

Figure 6.4 Variations of $\frac{N_x}{c_0} (C_{K^+} + C_{Na^+}) Q + Q^{2/3}$ as a function of $y N_x \alpha$ for

(a) HASE-20-80-2 at different salt concentrations, [KCl] and (b) HASE-20-80 with different cross-linked density at salt concentration of 100mM KCl. The master curve is represented by the solid line.

6.4 STEADY SHEAR VISCOSITY DEPENDENCE ON DEGREE OF NEUTRALIZATION

Figure 6.5(a) shows a plot of shear viscosity versus shear rate of four different salt concentrations (in mM KCl) of HASE-20-80-2 at 5 wt% polymer concentration and $\alpha = 1$. At low salt environment, microgel particles are highly swollen as shown in Figure 6.1(a), thus exhibiting large viscosity and significant shear-thinning behavior due to enhanced interaction between particles. With increasing salt concentration from 0.1 to 100 mM, the viscosity and shear-thinning behavior reduces and becomes almost independent of shear rate when $[KCl] > 10$ mM because the interaction between particles is less significant and the equilibrium position of the particles is less perturbed even at high shear rates.

Figure 6.5(b) depicts the low-shear relative viscosity, $\eta_r(\eta_0/\eta_s)$ versus the degree of neutralization, α for four different salt concentrations (in mM KCl) of HASE-20-80-2 at 5 wt% polymer concentration. The low shear rate viscosity plateau, η_0 was determined from a regression fit to the Cross model (Equation (4.1)) and the model fittings are represented by the solid lines in Figure 6.5(a). We observed that at $\alpha = 0$, where the colloidal particles are in the form of a compact sphere, the viscosities for all microgel systems are nearly identical to the viscosity of water (i.e. solvent), where $\eta_r \sim 1$. The viscosity increases continuously as α increases from 0 to 1.0 and microgels in low salt environment exhibits the largest viscosity increase for a fixed amount of neutralized carboxylate groups (or same neutralization degree).

Similar trend is observed where the viscosity begins to increase at a faster rate as reflected by the sharp increase in η_r at $\alpha > 0.4$, which further points to a transition region reflecting the conformational change of microgel particles during the neutralization process, as discussed earlier. Hence, salt concentration has significant impact on the inter-particle interaction between swollen microgel particles, which is attributed to the charge shielding effect of the counter ions (salt) on the negatively charged carboxylate groups, thus reducing the osmotic pressure inside the swollen particle.

Figure 6.5 (a) Shear viscosity, η versus shear rate, $\dot{\gamma}$ of four different salt concentrations (mM KCl) of HASE-20-80-2 at 5 wt% polymer concentration and $\alpha = 1$. (b) Low-shear relative viscosity, $\eta_r (\eta_0 / \eta_s)$ versus the degree of neutralization, α for four different salt concentrations (mM KCl) of HASE-20-80-2 at 5 wt% polymer concentration.

6.5 DYNAMIC VISCOELASTICITY

The frequency dependence of storage and loss modulus, G' and G'' respectively, was determined in low amplitude oscillatory shear experiments. Figure 6.6 shows the storage and loss modulus, G' and G'' as a function of frequency, ω for four different salt concentrations (in mM KCl) of HASE-60-40-4 at 5 wt% polymer concentration and $\alpha=1$. At low salt concentrations ($[KCl] < 10$ mM), the samples behave as viscoelastic solid and the storage modulus is larger than the loss modulus over the whole frequency range. The swollen microgel particles possess strong inter-particle interactions that imparts significant viscoelasticity and G' is independent of frequency and corresponds to the plateau modulus, G_p .

Figure 6.6 Storage modulus, G' and loss modulus, G'' as a function of angular frequency, ω for four different salt concentrations (mM KCl) of HASE-40-60-4 at 5 wt% polymer concentration and $\alpha=1$.

Increasing salt concentrations, ($[KCl] > 10$ mM), the samples change to a viscoelastic liquid with $G' < G''$ and the loss modulus approaches the asymptotic behavior of $G'' \propto \omega$. The plateau modulus, G_p decreases with salt concentration and a master-curve (represented by the solid line) was obtained when G_p was plotted against ϕ_{eff} as depicted in Figure 6.7.

Figure 6.7 Plateau modulus, G_p as a function of effective volume fraction, ϕ_{eff} for four different salt concentrations, mM KCl of HASE-40-60-4 at 5 wt% polymer concentration and $\alpha = 1$. The solid line represents the master-curve and the dotted line is to illustrate the two different regions of viscoelasticity.

Similar to Section 5.3, the effective volume fraction of soft microgel particles at various particle concentrations was determined using the proposed semi-empirical approach, which will be explained in detailed in Chapter 7. Based on Figure 6.7, the plateau modulus G_p is a strong function of the effective volume fraction and the effect of pH-dependent swelling and ionic strength (salt concentrations) on the modulus is minimized when ϕ_{eff} was used as the concentration variable.

The master curve obtained closely resembles the form of the Krieger- Dougherty (K-D) model (Equation (2.3)), where G_p (which is also a function of the particles interaction potential) increases exponentially at maximum volume fraction, $\phi_m \sim 0.63$. This is another evident that the generalized approach (details will be given in Chapter 7) is able to capture the physics of soft microgel particles at varying conditions, i.e. varying α and salt concentrations. From Figure 6.6, we observed two distinct regions of viscoelasticity, where the particles behave as viscoelastic liquid, $G' < G$ at $\phi_{\text{eff}} < 0.55$ and viscoelastic solid, $G' > G$ at $\phi_{\text{eff}} > 0.55$.

6.6 SUMMARY

It has been demonstrated experimentally that the particle size and viscosity of this microgel system decreases when salt is added. Experimental evidences suggest that not all the counter-ions from the salt, K^+ remains mobile in the solvent environment but some of these ions can penetrate the porous microgel particles to shield the negatively charged carboxylate groups and consequently some of the Na^+ counter-ions inside the particles are expelled, which reduces the osmotic pressure inside the microgels. We have successfully expanded the theoretical scaling law, $Q \propto (y \alpha N_x)^{3/2}$ to include new data containing microgel systems with varying salt concentrations $[KCl]$. Excellent agreement was obtained, where all the data fall on a master curve, and this confirmed that $\frac{N_x}{c_0} (C_{K^+} + C_{Na^+}) Q + Q^{2/3}$ is proportional to $y N_x \alpha$ as predicted from Equation (6.4).

7 SEMI-EMPIRICAL APPROACH FOR MODELLING CHARGED SOFT MICROGEL PARTICLES

In Chapters 4, 5 and 6, we manipulate the characteristics of microgel particles and their corresponding interaction potential by varying the followings; (a) degree of neutralization of MAA groups, α , (b) salt concentrations, (c) microgel cross-linked density, and (d) molar ratio of MAA-EA. We observed that such changes do have a significant impact on the microgel particle size and their bulk rheological property. These interesting findings have motivate us to propose a semi-empirical approach for predicting the viscosity of dilute and concentrated soft condensed particles, by taking into account the physics of compressible soft microgel particles and the description of this approach will be given in this chapter.

7.1 RHEOLOGICAL BEHAVIOR

Figures 7.1(a) to 7.1(d) display the flow properties of four different microgel systems, namely; (a) neutralization degree (α) of MAA groups; (b) salt concentration; (c) microgel cross-linked density; and (d) molar ratio of MAA groups. At low α (< 0.5), high salt environment, high cross-linked density and low content of MAA, the samples display a Newtonian behavior with a low shear viscosity close to that of water. The effective volume, ϕ_{eff} of the microgels in solution is small due to insignificant degree of swelling.

At large α (> 0.5), low salt environment ($< 10\text{mM}$), low cross-linked density ($< 2\text{wt}\%$), and high content of MAA (> 30 mole %), the enhanced osmotic pressure exerted by the counter-ions trapped inside the polymeric network by the large number of charged carboxylate groups causes an increase in the effective volume, ϕ_{eff} occupied by the particles. Such increase essentially decreases the inter-particle distance, where the interaction forces between the swollen particles increase sharply, resulting in the shear-thinning behavior. The low shear viscosity can change by more than three orders of magnitude, for example, 5 wt% microgel particles at $\alpha = 1$ possesses a low shear viscosity of ~ 0.006 Pa.s at 0 wt% DAP and it increases to ~ 11 Pa.s at 1 wt% DAP. The low shear rate viscosity plateau, η_0 was determined from a regression fit to the Cross model (Equation (4.1)) and are represented by the solid lines in Figure 7.1.

Figure 7.1 Relative viscosity versus shear rate of cross-linked MAA-EA microgel at 5wt% polymer concentration and four different conditions; (a) varying neutralization degree, α of HASE-20-80-2 in salt free solution; (b) varying salt concentration of HASE-20-80-2 at $\alpha=1$; (c) varying cross-linked density of microgels with 20 mole % MAA in salt free solution and at $\alpha=1$; and (d) varying molar ratio of MAA groups of 4wt% cross-linked microgels in salt free solution and at $\alpha=1$. The solid lines denote mathematical fittings according to Equation (4.1).

7.2 MODELLING SOFT PARTICLES USING A CONSTANT SPECIFIC VOLUME, k

Similar to the approach proposed by Ballauff and co-workers, the effective volume fraction of this pH-responsive microgel system was determined using the Batchelor's equation. Intrinsic viscosity measurements were conducted for all the four different systems and a constant specific volume, k was determined based on Equation (2.21),

$$\frac{\eta_0}{\eta_s} = 1 + 2.5(kc) + 5.9(kc)^2 ,$$

for each system at α ranging from 0 to 1. The relative viscosity of dilute HASE-20-80-2 is shown in Figure 7.2 as a function of mass concentration, c for different α s. The solid lines represent the model fittings according to Equation (2.21) where $\phi_{\text{eff}} = kc$.

Figure 7.2 Relative viscosity versus polymer concentration, c of HASE-20-80-2 at six different neutralization degrees. Solid lines represent fits according to Equation (2.21).

Table 7.1 compares the specific volume, k obtained from viscometric and the corresponding R_h from dynamic light scattering (DLS) measurements for HASE-20-80-2 system in three different salt concentrations. Both measurements were conducted in the dilute region, where k describes the volume change of microgel particles. The ratios, $k(\alpha)/k(\alpha=0)$ and $[R_h(\alpha)/R_h(\alpha=0)]^3$ are in excellent agreement, confirming the validity of the parameter k in describing the volume change, and ϕ_{eff} adequately describes the effective hydrodynamic volume of microgel suspension in dilute solution.

α	R_h (nm)	R_g (nm)	k	$[R_h(\alpha)/R_h(\alpha=0)]^3$	$k(\alpha)/k(\alpha=0)$
0.1 mM KCl					
0.0	40.5	43.6	1.58	1.00	1.00
0.5	96.0	100.2	19.20	13.32	12.31
0.8	112.8	121.6	34.00	21.61	21.79
1.0	116.0	128.0	37.60	23.50	24.10
10 mM KCl					
0.0	37.5	41.2	1.55	1.00	1.00
0.5	75.0	75.8	11.20	8.00	7.20
0.8	87.5	92.0	19.20	12.70	12.30
1.0	90.5	96.4	22.00	14.06	14.10
100 mM KCl					
0.0	32.5	38.0	1.52	1.00	1.00
0.5	45.0	52.3	3.60	2.65	2.37
0.8	52.0	61.8	7.20	4.10	4.74
1.0	57.0	64.0	8.80	5.39	5.80

Table 7.1 Results for dynamic light scattering and viscometric measurements of dilute HASE-20-80-2 at different α and salt concentrations.

Conversely, the relative viscosity can also be predicted from light scattering measurement based on the data in Table 7.1 for a known particle concentration at varying α s. Obviously, the viscosity measurement is simpler and thus, is commonly the preferred method. Also, the intrinsic viscosity, $[\eta]$ data allows the determination of the radius of gyration, R_g from the relationship $[\eta]\bar{M}_w = \frac{10}{3} \pi N_A R_g^3$ where the molecular weight $\bar{M}_w$ was determined from static light scattering technique. The values of R_g are given in Table 7.1, which gives information on the molecular properties of the microgels.

In the unneutralized state ($\alpha = 0$), the specific volume, k for the different systems is approximately 1.55, which is slightly larger than 1.0 observed for model hard spheres. This suggests that the microgel systems are not ideal hard spheres but correspond very close to that of model hard spheres.

In Figure 7.3, the relative viscosity of HASE-20-80-2 in four different salt concentrations was plotted against the effective volume fraction, ϕ_{eff} calculated from the constant k determined from Figure 7.2. For $\phi_{\text{eff}} < 0.3$, all the relative viscosity data obey the Batchelor's equation for hard sphere shown in Equation (2.20),

$$\eta_0/\eta_s = 1 + 2.5\phi_{\text{eff}} + 5.9\phi_{\text{eff}}^2,$$

when ϕ was replaced by ϕ_{eff} . This suggests that at dilute region, $\phi_{\text{eff}} < 0.3$, k is independent of polymer concentration. When $\phi_{\text{eff}} > 0.3$, the viscosity data deviate from the Batchelor's prediction, confirming that the specific volume, k determined at dilute solution regime is not valid at moderate to high concentrations.

As the microgel particles become larger (R_h increases from 96 to 116 nm when α changes from 0.5 to 1.0, as shown in Table 7.1 for 0.1 mM KCl) the K-D model (Equation (2.3)),

$$\eta_0/\eta_s = (1 - \phi/\phi_m)^{-[\eta]\phi_m}$$

cannot predict the changes in the relative viscosity and ϕ_m can be as high as 1.5. The failure in the K-D model in predicting the viscosity of “soft” colloidal particles lies in the fact that the specific volume, k could not account for the prevailing physics at higher volume fraction.

Figure 7.3 Relative viscosity versus ϕ_{eff} of microgel system (HASE-20-80-2). (a) Dilute solution region at four different salt concentrations, $[KCl]$ ($\triangle$:0.1 mM; $\square$:1 mM; $\circ$:10 mM; $\diamond$:100 mM) and three different α s ; $\alpha=0.5$ (grey), $\alpha=0.8$ (open) and $\alpha=1.0$ (black). Dark solid line denotes Batchelor's equation (Equation (2.20)) (b) Dilute to concentrated region at salt concentration of 0.1 mM KCl for three α s, ($\triangle$: $\alpha=0.5$; Δ : $\alpha=0.8$; $\blacktriangle$: $\alpha=1.0$). Dotted line denotes the K-D model (Equation (2.3)).

7.3 MODELLING SOFT PARTICLES USING A VARIABLE SPECIFIC VOLUME, k

It is postulated that inter-particle distance decreases with increasing concentration of soft particles. At a critical particle concentration, the concentration of free counter-ions in the solution can be large enough to induce osmotic de-swelling of soft particles resulting in the shrinkage of the particles. This hypothesis is confirmed by the observed reduction in particle size and k (Table 7.1) when increasing amounts of salts were added. Based on this physical insight, we anticipate that the specific volume, k should be a function of volume fraction of particles. A pictorial representation on the changes in the specific volume k is given in Figures 7.4(a) to 7.4(c), where k should decrease with increasing microgel concentrations.

Figure 7.4 A pictorial representation of the changes in the specific volume k at three different concentration regimes; (a) dilute; (b) semi-dilute; and (c) concentrated region.

Figure 7.4(a) illustrates the soft microgel particle in the swollen state. Unlike hard spheres, cross-linked microgel particles are impregnated with large amounts of solvent, rendering them to be “soft” and porous. In the dilute solution regime, inter-particle interaction is absent and k is a constant. With increasing concentration, the inter-particle distance between microgel particles is reduced and the concentration of free counter-ions in the solution can be large enough to induce an osmotic de-swelling of soft particles (Figure 7.4(b)). Increasing inter-particle interactions cause the microgel to shrink resulting in a corresponding decrease in k , until it approaches the hard sphere limit (described by the black core). If we do not take into account the changes in the specific volume k , overlap of the electro-viscous layer of soft particles (Figure 7.4(c)), and $\phi_{\text{eff}} = kc$ will exceed the maximum packing limit of 0.63 and can even approach 1.5 as depicted in Figure 7.3(b).

A generalized semi-empirical approach is proposed to model soft condensed particles by taking into account the physics of compressible soft microgel particles where k is inversely proportional to volume fraction. The specific volume, k depends on concentration of particles (c), neutralization degree (α) of the acid groups (MAA), salt concentration $[KCl]$, microgel cross-linked density (wt% DAP) and molar ratio of acid groups (% MAA), i.e., $k = f(c, \alpha, [KCl], \text{wt\% DAP}, \% \text{ MAA})$. The values of k were determined from the mathematical fitting of the data to the form of the modified Krieger-Dougherty equation shown in Equation (2.22),

$$\frac{\eta_0}{\eta_s} = \left(1 - \frac{kc}{\phi_m}\right)^{-[\eta]\phi_m}.$$

Figure 7.5 Specific volume, k as a function of concentration of cross-linked MAA-EA microgel at 5wt% polymer concentration and four different conditions; (a) varying neutralization degree, α of HASE-20-80-2 in salt free solution; (b) varying salt concentrations (mM KCl) of HASE-20-80-2; (c) varying cross-linked density (wt% DAP) of microgels with 20 mole % MAA in salt free solution; and (d) varying molar ratio of MAA groups (% MAA) of 4wt% cross-linked microgels in salt free solution. The solid lines denote mathematical fittings according to Equation (7.1).

Figures 7.5(a) to 7.5(d) show the specific volume, k as a function of concentration of particles for four different systems, namely; (a) degree of neutralization (α) of MAA groups; (b) salt concentration $[KCl]$; (c) microgel cross-linked density; and (d) molar ratio of MAA groups. The general trend of specific volume, k can be described by a mathematical expression given in Equation (7.1),

$$\frac{k - k_{\min}}{k_0 - k_{\min}} = \left[1 + \left(\frac{c}{c'} \right)^2 \right]^{-m} \quad (7.1)$$

with $k_{\min}$ describes the limiting condition when the soft particles are compressed to the hard sphere equivalent volume at high concentration. Microgel particles are highly swollen at large α , low salt environment, low cross-linked density and high content of MAA. Such particles exhibit strong dependence of k on particle concentration, where (k/k_0) may decrease from 1.0 to 0.2.

The constant c' denotes the critical concentration at which the concentration of free counter-ions in the solution is large enough to induce an osmotic de-swelling of the soft particle resulting in a smaller k . The rate of decrease in k with particle concentration is described by the parameter m , which can also be obtained from the slope of $\frac{k - k_{\min}}{k_0 - k_{\min}}$ versus c curve on a log-log plot. Depending on the nature of soft particles and surrounding environment, the rate of decrease in k with particle concentration varies.

Figures 7.6(a) and 7.6(b) summarize the dependence of c' and m on neutralization degree, α and salt concentrations of HASE-20-80-2 microgel determined from the mathematical fitting of the data to Equation (7.1).

Figure 7.6 (a) c' (filled symbols) and (b) m (open symbols) as a function of degree of neutralization, α of HASE-20-80-2 microgel system at four different salt concentrations, [KCl]; (Δ :0.1 mM; $\square$:1 mM; $\circ$:10 mM; $\diamond$:100 mM).

As neutralization degree, α increases and salt concentration reduces, c' decreases and m increases because the enhanced osmotic pressure causes the microgel particles to swell further, which decreases the inter-particle distance resulting in an increase in the interaction forces between the swollen particles. Thus, the critical concentration, c' at which the soft particle starts to shrink decreases and the rate of shrinkage, m increases. At low salt environment (e.g 0.1 mM KCl), the critical shrinkage concentration, c' decreases from 3 to 1 wt% ($\sim$ three times) when neutralization degree, α is increased from 0 to 1. Correspondingly, the rate of shrinkage, represented

by the slope, m increases by ~ 10 times (i.e. from 0.03 to 0.33) when neutralization degree, α is increased from 0 to 1.

To further describe the rate of decrease in k with c for the four different systems, Equation (7.1) can be differentiated with respect to c to give Equation (7.2) and the dependence of $\frac{\partial k}{\partial c}$ as a function of concentration of cross-linked MAA-EA microgel is shown in Figure 7.7 at four different conditions; (a) varying α ; (b) varying salt concentrations; (c) varying microgel cross-linked density; and (d) varying molar ratio of MAA groups.

$$\frac{\partial k}{\partial c} = - \frac{2m(k_0 - k_{\min})}{c'^2} \left[1 + \left(\frac{c}{c'} \right)^2 \right]^{-(m+1)} \quad (7.2)$$

We observed that $\frac{\partial k}{\partial c}$ increases up to a maximum rate that corresponds to c' beyond which it decreases gradually as the soft particles approach the limiting hard sphere equivalent volume. The negative sign indicates that k is decreasing with respect to c . The maximum in $\frac{\partial k}{\partial c}$ increases with respect to the following conditions; i.e. higher α , lower salt concentration, lower cross-linked density and higher content of MAA as depicted by the solid lines in Figures 7.7(a), 7.7(b), 7.7(c) and 7.7(d) respectively. The microgel particles are highly swollen and exhibit strong inter-particle interactions at these conditions. The maximum in $\frac{\partial k}{\partial c}$ can change by more than five times, for example, fully neutralized ($\alpha=1$) microgel particles possesses a $\frac{\partial k}{\partial c}$ of $\sim 500 \text{ ml/g}^2$ at 20 mole % MAA and it increases to $\sim 3000 \text{ ml/g}^2$ at 50 mole % MAA.

Figure 7.7 $\partial k/\partial c$ as a function of concentration of cross-linked MAA-EA microgel at 5wt% polymer concentration and four different conditions; (a) varying neutralization degree, α of HASE-20-80-2 in salt free solution; (b) varying salt concentrations (mM KCl) of HASE-20-80-2; (c) varying cross-linked density (wt% DAP) of microgels with 20 mole % MAA in salt free solution; and (d) varying molar ratio of MAA groups (% MAA) of 4wt% cross-linked microgels in salt free solution. The solid lines are to guide the eye, which shows the increasing trend of m and the reducing trend of c' as the conditions vary.

The maximum point observed in Figure 7.7 further confirms our hypothesis which suggests a change in conformation of the microgel particles with increasing volume fraction. The osmotic pressure exerted by the counter-ions trapped in the microgel retains the existing particle conformation, whereas the free counter-ions in the solution induce an osmotic de-swelling on the particle. Consequently, a critical concentration, c' reflecting the conformational change of microgel particles caused by the competition of these two kinds of interactions is observed.

Below this critical concentration (i.e. the dilute solution regime), the rate of reduction in specific volume, k with concentration is small because the osmotic de-swelling induced by the free counter-ions in the solution is insufficient to overcome the osmotic pressure exerted by the counter-ions trapped inside the microgel particles. When c' is reached, the osmotic de-swelling force becomes sufficiently strong in overcoming the osmotic pressure inside the soft particles. Solvent is expelled from the swollen particles and the particle shrinks resulting in a corresponding maximum rate of decrease in k . Beyond c' , the concentration of free counter-ions in the solution is further increased, which causes k to decrease but at a slower rate as the hard sphere limit is approached.

The effective volume fraction of soft microgel particles at various particle concentrations can be determined from Equation (7.3) by substituting Equation (7.1) into $\phi_{\text{eff}} = k c$,

$$\phi_{\text{eff}} = k_{\min} + (k_0 - k_{\min}) \left[1 + \left(\frac{c}{c'} \right)^2 \right]^{-m} * c . \quad (7.3)$$

Figure 7.8 Relative low shear viscosity versus effective volume fraction of cross-linked MAA-EA microgel at 5wt% polymer concentration and four different conditions; (a) varying neutralization degree, α of HASE-20-80-2 in salt free solution; (b) varying salt concentrations (mM KCl) of HASE-20-80-2; (c) varying cross-linked density (wt% DAP) of microgels with 20 mole % MAA in salt free solution; and (d) varying molar ratio of MAA groups (% MAA) of 4wt% cross-linked microgels in salt free solution. The solid line and the dotted line denote the hard sphere behavior according to Equation (2.20) and Equation (2.3) respectively.

This expression corrects for the changes in the volume fraction of soft particles to that of equivalent hard sphere. Excellent agreement with the K-D model prediction was observed for moderate to high volume fraction where a common curve was obtained when the viscosity data were plotted using the modified ϕ_{eff} determined from Equation (7.3) (Figures 7.8(a) to 7.8(d)). This strongly suggests that the generalized approach is able to capture the physics of soft microgel particles and the form of Equation (7.3) has the capability of predicting the relative viscosity of different systems. Good agreement with the Batchelor's equation is evident (see insets of Figures 7.8(a) to 7.8(d)) at volume fraction less than 0.1.

Table 7.2 summarizes the fitted parameters k_0 , c' , and m for all the four systems discussed, which were obtained by fitting Equation (7.1) onto the data of Figures 7.5(a) to 7.5(d). [Note: The fitted parameters of HASE-20-80-2 microgel are not included as they were already presented in Figures 7.6(a) and 7.6(b)]. These tabulated parameters are useful as it permits the determination of k from Equation (7.1) for any known microgel concentration, c of a particular system. When k is known, ϕ_{eff} can be determined from Equation (7.3) and hence the relative viscosity can be predicted by the K-D model (Equation (2.22)). This semi-empirical model provides us with the capability to predict the viscosity, and describing the physics of compressibility of soft particles as a function of particle concentration.

α	k_0 (ml/g)	c' (g/ml)	m
HASE-20-80-1 at 0.1 mM KCl			
0.0	1.941	0.030	0.042
0.5	26.196	0.017	0.260
0.8	46.900	0.012	0.425
1.0	56.852	0.008	0.452
HASE-20-80-3 at 0.1 mM KCl			
0.0	1.520	0.032	0.030
0.5	12.625	0.021	0.142
0.8	25.022	0.015	0.274
1.0	30.910	0.012	0.305
HASE-20-80-4 at 0.1 mM KCl			
0.0	1.450	0.033	0.020
0.5	9.411	0.023	0.118
0.8	21.247	0.016	0.237
1.0	25.661	0.014	0.283
HASE-30-70-4 at 0.1 mM KCl			
0.0	1.998	0.028	0.030
0.5	18.962	0.020	0.154
0.8	29.923	0.015	0.294
1.0	37.829	0.013	0.343
HASE-40-60-4 at 0.1 mM KCl			
0.0	2.021	0.025	0.041
0.5	22.955	0.016	0.182
0.8	34.907	0.012	0.323
1.0	47.025	0.009	0.366
HASE-50-50-4 at 0.1 mM KCl			
0.0	2.051	0.023	0.059
0.5	26.169	0.012	0.205
0.8	44.369	0.010	0.359
1.0	62.270	0.007	0.385

Table 7.2 Summary of the fitted parameters k_0 , c' , and m for all the four systems discussed; neutralization degree (α) of MAA groups, salt concentration, microgel cross-linked density, and molar ratio of MAA groups.

7.4 SUMMARY

A semi-empirical approach that is applicable for describing the flow behavior of soft condensed matter, which can then be used to predict the viscosity behavior of dilute and concentrated soft sphere systems has been successfully developed. The classical approach where specific volume, k is a constant determined at dilute solution regime, could not account for the prevailing physics at higher volume fraction. Instead, a variable specific volume, k was introduced to convert the mass concentration to effective volume fraction where k is defined by the mathematical expression,

$$\frac{k - k_{\min}}{k_0 - k_{\min}} = \left[1 + \left(\frac{c}{c'} \right)^2 \right]^{-m}.$$

The present model possesses very few constants (k_0 , c' , and m), yet it has good predictive capability. The utility of the new approach was tested against four different systems and excellent agreement was obtained.

8 THEORETICAL APPROACH FOR MODELLING CHARGED SOFT MICROGEL PARTICLES

In Chapter 7, a semi-empirical approach for predicting the viscosity of dilute and concentrated systems was proposed, where a variable specific volume, k was introduced to convert the mass concentration, c to effective volume fraction, ϕ_{eff} . The validity of the new approach is then compared against the theoretical approach originally proposed by Cloitre and co-workers [Cloitre et al., 2003] (Section 2.5.3) and the description is given in this chapter.

8.1 EFFECT OF FREE COUNTER-IONS ON VISCOSITY

8.1.1 DETERMINATION OF FRACTION OF FREE COUNTER-IONS USING CALCULATION METHOD

The theoretical approach developed by Cloitre and co-workers [Cloitre et al., 2003] considers the osmotic de-swelling phenomenon of the microgels at high particle concentrations, induced by the large amount of free counter-ions in the solution. They showed that the volume of microgels can be reduced by one third near close packing ($\phi = 0.6$) and thus it is critical to use the swelling ratio at finite concentration, $\tilde{Q}$ to calculate the volume fraction of microgels as given in Equation (2. 27),

$$\phi = \frac{\tilde{Q}}{V_m c_0} \frac{\rho_s}{\rho_p} c .$$

The variations of the relative swelling of the microgels with cross-linked densities, N_x , molar fraction of acid (MAA) units, y and the degree of neutralization, α were determined and agreed with the theoretical scaling law $Q \propto (y\alpha N_x)^{3/2}$ as described in Chapters 4 and 5. The viscosity data of our pH-responsive MAA-EA microgel system shown in Figures 7.8(a), 7.8(c) and 7.8(d) were replotted in Figures 8.1 using the effective volume fraction, ϕ_{eff} computed from Equation (2.27) where the values $\tilde{Q}$ were determined from the swelling ratio (Equation (2.26)),

$$\frac{\tilde{Q}}{Q} = \left[1 - \frac{\Gamma}{1 - \phi} \right]^{3/2} .$$

The fraction of counter-ions that can leave the microgels and diffuse in the solution, Γ were calculated from the Debye length (Equation (2.23)),

$$\kappa_{\text{in}}^{-1} = (4 \pi l_B N_A C_{\text{in}})^{-1/2} ,$$

which is then substituted into (Equation (2.24) to obtain Γ ,

$$\Gamma \cong 3 \kappa_{\text{in}}^{-1} / R_h .$$

The values for each system at infinite dilution are shown in Figure 8.2 (solid symbols). Data from Figure 7.8(b) were not considered as the derivation of Equation (2.26), is only applicable for salt free solutions.

It is observed that the data agrees with the prediction from the K-D model (Equation (2.3)),

$$\frac{\eta_0}{\eta_s} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

for microgel systems with low α , high cross-linked densities and low MAA content, i.e. HASE-20-80-3 (Figure 8.1(c)) and HASE-20-80-4 (Figure 8.1(d)). The viscosity data deviates from the K-D model for microgels with large swelling ratio at high volume fraction ($\phi > 0.5$), which suggests that Γ calculated from the Debye length (Equation (2.23) and (2.24)) determined at dilute solution regime is not valid at moderate to high concentrations. It is known that osmotic de-swelling prevails at high solid concentration, thus particle size, R_h no longer remains a constant.

Figure 8.1 Relative low shear viscosity versus effective volume fraction determined from Equation (2.27) where Γ was calculated from Equation (2.23) and (2.24) for cross-linked MAA-EA microgel systems with varying cross-linked densities; (a) HASE-20-80-1, (b) HASE-20-80-2, (c) HASE-20-80-3 and (d) HASE-20-80-4 and varying MAA content; (e) HASE-40-60-4 and (f) HASE-50-50-4 at three different α s ($\triangle$: $\alpha=0.5$; $\square$: $\alpha=0.8$; $\circ$: $\alpha=1.0$). The solid line denotes the hard sphere behavior according to Equation (2.3).

8.1.2 DETERMINATION OF FRACTION OF FREE COUNTER-IONS USING EXPERIMENTAL MEASUREMENTS

A more accurate method to determine Γ is to measure the concentration of free counter-ions as a function of microgel concentration using the sodium (Na^+) ion-selective electrode (ISE). Measurements were conducted for each systems and Figure 8.2 compares the values of Γ measured using ISE with the values calculated from Equation (2.23) and (2.24) for microgel systems with low cross-linked densities, i.e., HASE-20-80-1 (Figure 8.2(a)) and HASE-20-80-2 (Figure 8.2(b)) and high MAA content, i.e., HASE-40-60-4 (Figure 8.2(c)) and HASE-50-50-4 (Figure 8.2(d)).

It is observed that Γ increases with microgel concentration, thus the assumption that the variations of Γ with the swelling ratio ($\Gamma \sim Q^{1/6}$) is small at infinite dilution [Cloitre et al., 2003], is no longer valid at higher microgel concentration. As discussed earlier, microgel particles are highly swollen at large α , low cross-linked density and high content of MAA. Such particles exhibit strong dependence of Γ on particle concentration, where Γ may increase from 0.04 to 0.2 when concentration is increased from 0.1 wt% to 4 wt% (Figure 8.2(d)). The larger fraction of free counter-ions, Γ results in stronger osmotic de-swelling effect as described by Equation (2.26),

$$\frac{\tilde{Q}}{Q} = \left[1 - \frac{\Gamma}{1 - \phi} \right]^{3/2},$$

which confirms the earlier hypothesis that the specific volume, k should decrease with increasing microgel concentration.

Figure 8.2 Comparison of values of Γ measured using Na^+ ISE (filled symbols) with the values calculated from the Debye length (Equation (2.23) and (2.24)) (open symbols) at three different α s (Δ : $\alpha=0.5$; $\square$: $\alpha=0.8$; $\bigcirc$: $\alpha=1.0$) for microgel systems with low cross-linked densities; (a) HASE-20-80-1 and (b) HASE-20-80-2 and high MAA content; (c) HASE-40-60-4 and (d) HASE-50-50-4.

Figure 8.3 displays the corrected viscosity data where ϕ_{eff} was determined from Equation (2.27) using Γ measured by ISE as shown in Figure 8.2. Within the experimental accuracy, the data agrees well with the K-D model (Equation (2.3)) for dilute to high volume fraction, unlike the deviation observed when Γ was calculated from Equations (2.23) and (2.24) (open symbols). It is critical to use Γ measured at different concentrations instead of those determined by Equations (2.23) and (2.24), as this will lead to an overestimation of the volume fraction as evident by the data in Figures 8.1.

Figure 8.3 Relative low shear viscosity versus effective volume fraction calculated from Equation (2.27) for cross-linked MAA-EA microgel systems with varying cross-linked densities; (a) HASE-20-80-1, (b) HASE-20-80-2 and varying MAA content; (c) HASE-40-60-4 and (d) HASE-50-50-4 at three different α s ($\triangle$: $\alpha=0.5$; $\square$: $\alpha=0.8$; $\circ$: $\alpha=1.0$). The open symbols represent ϕ_{eff} determined when Γ was calculated from Equation (2.23) and (2.24) whereas the filled symbols represents ϕ_{eff} calculated from the values of Γ measured using Na^+ ISE. The solid line denotes the hard sphere behavior according to Equation (2.3).

8.2 COMPARISON OF SEMI-EMPIRICAL AND THEORETICAL APPROACH

Figure 8.4 shows a comparison of ϕ_{eff} determined using the semi-empirical approach (open symbols) proposed by our group (Equation (7.3)),

$$\phi_{\text{eff}} = k_{\min} + (k_0 - k_{\min}) \left[1 + \left(\frac{c}{c^*} \right)^2 \right]^{-m} * c$$

with the theoretical approach (closed symbols) proposed by Cloitre and co-workers (Equation (2.27)),

$$\phi_{\text{eff}} = \frac{\tilde{Q}}{V_m c_0} \frac{\rho_s}{\rho_p} c$$

for two microgel systems, HASE-20-80-1 and HASE-50-50-4. The ϕ_{eff} determined from these two methods are in good agreement, and strongly suggests that the semi-empirical approach is able to capture the physics of soft microgel particles and the form of (Equation (7.3)) has the capability of predicting the relative viscosity of different systems.

Figure 8.4 Comparison of values of ϕ_{eff} determined using the semi-empirical approach (Equation (7.3)) (open symbols) with the theoretical approach (Equation (2.27)) where values of Γ was measured using Na^+ ISE (filled symbols) of microgel systems; (a) HASE-20-80-1 and (b) HASE-50-50-4 at two different α s (Δ : $\alpha=0.5$; $\circ$: $\alpha=1.0$).

8.3 SUMMARY

The significant breakthrough presented here is the excellent agreement obtained for four different microgel systems, where our proposed semi-empirical approach was compared against a theoretical model. This is important evidence that the present model is valid for describing the physics of soft particles, which can then be used to predict the viscosity behavior of dilute and concentrated soft sphere systems.

9 A TURBIDITY STUDY OF SOFT MICROGEL PARTICLES IN COLLOIDAL SUSPENSIONS

In Chapters 7 and 8, the data of specific volume, k and swelling ratio at finite concentration, $\tilde{Q}$ strongly implies that microgel particles undergo osmotic deswelling with increasing particle concentration where the volume of microgels can reduce significantly depending on the nature of soft particles and surrounding environment. Thus, knowledge of structural properties of microgels is of technical importance since they are intimately connected to the particle interaction potentials. Understanding of these parameters permits us to have a quantitative evaluation of the factors governing particle osmotic compressibility as well as the flow behavior of these systems.

9.1 STRUCTURE FACTORS FROM TURBIDIMETRY

As discussed in Section 2.7, turbidimetry is well suited to study the structure factors of dilute and concentrated colloidal suspensions, as this method is practically insensitive towards multiple scatterings. Figure 9.1(a) displays the transmittance as a function of wavelength, λ obtained from turbidity measurements, for six different microgel concentrations of HASE-20-80-2 in 10 mM KCl solution. The transmittance, T is defined as I_t/I_0 with I_0 being the incident intensity of the light and I_t the

transmitted intensity. With increasing microgel concentration, the transmitted intensity of light decreases at a particular light wavelength and hence the turbidity of the suspension calculated from Equation (2.34),

$$\tau = l^{-1} \ln(I_0 / I_t),$$

increases as demonstrated in Figure 9.1(b).

Figure 9.1 Turbidity measurements obtained from UV-visible spectroscopy for six different microgel concentrations of HASE-20-80-2 in salt free solution and $\alpha = 1$. (a) Transmittance, I_t/I_0 as a function of wavelength, λ , and (b) turbidity, τ as a function of wavelength, λ .

The method of Ballauff et al. [Apfel, 1995 ; Weiss, 1996 ; Horner, 1997] described in Section 2.7.1 was employed to extract the particle osmotic compressibility contribution to the structure factor from the turbidity data in Figure 9.1. Figure 9.2 displays a plot of specific turbidity, τ/c as a function of c at fixed wavelength, λ of

HASE-20-80-2 at $\alpha=1$, where $Z(\lambda^2, c)$ can be calculated by (τ/c) values when the concentration was extrapolated to zero as suggested by Equation (2.42),

$$Z(\lambda^2, c) = \frac{(\tau/c)}{(\tau/c)_{c=0}}$$

The linear curve fittings given by the solid lines permits the intercept, $(\tau/c)_{c=0}$ to be extracted from Figure 9.2. The theoretical derivation given by Equations (2.39) to Equation (2.42) suggests that the specific turbidity (τ/c) will decrease due to inter-particle interaction and is directly proportional to c in the region of low c . The experimental values of (τ/c) as a function of c corroborate this analysis as evident in Figure 9.2 and this plot is appropriate for the extrapolation of (τ/c) to vanishing concentration.

Figure 9.2 Specific turbidity, τ/c as a function of microgel concentration, c at fixed wavelength, λ of HASE-20-80-2 in salt free solution and $\alpha=1$. The solid lines are the linear curve fits to the data to extract the intercept, $(\tau/c)_{c=0}$.

A plot of $Z(\lambda^2, c)$ as a function of $1/\lambda^2$ is then given in Figure 9.3, and the intercept of this plot at each concentration is the structure factor $S(0)$ (Equation (2.40)),

$$Z(\lambda^2, c) = S(0, c) + 0(1/\lambda^2),$$

which is proportional to the osmotic compressibility, κ_T from Equation (2.33),

$$S(Q=0) = \rho k T \kappa_T = k T (\delta\rho/\delta p)_T.$$

It measures the dispersion resistance to particle compression, where $S(0)$ decreases with increasing resistance when the concentration of particles becomes larger. The values of $S(0)$ ranges from $0 < S(0) < 1$ and $S(0) = 1$ when inter-particle interactions are negligible. The linear curve fits to the data to extract the intercept are given by the solid lines in Figure 9.3. As discussed in Section 2.7.1, since the diameter of the particles is around 150 nm and wavelengths used are greater than 500 nm, the approximations (Equation (2.39) and (2.40)) used in this technique are justified.

Figure 9.3 Integrated structure factor, $Z(\lambda^2, c)$ as a function of $1/\lambda^2$ at different microgel concentration, c of HASE-20-80-2 in salt free solution and $\alpha = 1$. The solid lines are the linear curve fits to the data to extract the intercept, which equals the structure factor of the colloidal particles in the zero angle limit ($S_{cc}(0)$).

9.2 STRUCTURE FACTORS AS A FUNCTION OF CROSS-LINKED DENSITY

Figure 9.4(a) displays a plot of $S_{cc}(0)$ of fully neutralized ($\alpha = 1$) microgels with 20 mole % MAA at three different cross-linked densities as a function of microgel concentration in salt free solution. In the dilute solution regime, inter-particle interaction is absent and the osmotic compressibility is fairly similar for microgels with different cross-linked densities.

With increasing concentration, the inter-particle distance between microgels is reduced, thus increasing the dispersion resistance to particle compression, which results in a corresponding decrease in osmotic compressibility. Microgels with similar amounts of charged carboxylate groups are more swollen at low cross-linked densities and the effective volume fraction, ϕ_{eff} occupied by the particles increases. Such increase essentially decreases the inter-particle distance and the interaction forces between the swollen particles increase sharply, resulting in a larger decrease in $S_{cc}(0)$ where $S_{cc}(0)$ may decrease from 1.0 to 0.3 for HASE-20-80-1 as seen in Figure 9.4(a).

The structure factor, $S_{cc}(0)$ of microgels with 20 mole% MAA at various cross-linked densities and particle concentrations was plotted against the effective volume fraction, ϕ_{eff} calculated from Equation (7.3),

$$\phi_{eff} = k_{min} + (k_0 - k_{min}) \left[1 + \left(\frac{c}{c_0} \right)^2 \right]^{-m} * c ,$$

when Equation (7.1) was substituted into $\phi_{\text{eff}} = k c$ as shown in Figure 9.4(b). All the data determined at different cross-linked densities seemed to fall onto a single master-curve, which clearly suggest that particle interaction potential and osmotic compressibility is a function of effective volume fraction of microgels.

Figure 9.4 Structure factor, $S_{cc}(0)$ of fully neutralized ($\alpha=1$) microgels with 20 mole% MAA in salt free solutions at three different cross-linked densities as a function of (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{\text{eff}} = k c$. The solid lines are to guide the eye, which shows the reducing trend of $S_{cc}(0)$ as the cross-linked densities vary.

9.3 STRUCTURE FACTORS AS A FUNCTION OF IONIC STRENGTH

Figure 9.5(a) shows a plot of $S_{cc}(0)$ versus microgel concentration of four different salt concentrations (in mM KCl) of HASE-20-80-2 at $\alpha = 1$. Similarly, in the dilute solution regime, inter-particle interaction is absent and the osmotic compressibility, $S_{cc}(0)$ is fairly similar for microgels in different salt environment. At low salt environment, microgel particles are highly swollen as shown in Figure 6.1(a), thus exhibiting large resistance to particle compression, which results in a lower $S_{cc}(0)$ due to enhanced interaction between particles with increasing solid concentrations.

With increasing salt concentration from 0.1 to 100 mM KCl, microgel particles experience osmotic de-swelling due to charged shielding effect from the salt counter-ions. The resistance to particle compression decreases and $S_{cc}(0)$ becomes almost independent of microgel concentration because the interaction between particles is less significant. At low salt environment (e.g 0.1 mM KCl), the structure factor, $S_{cc}(0)$ may decrease from 0.9 to 0.4 as seen in Figure 9.5(a) when microgel concentration is increased from 0.5 wt% to 2.5 wt%. On the other hand, the drop in $S_{cc}(0)$ is less significant i.e., from 0.9 to 0.6 when salt concentration increases to 100 mM KCl for the same microgel concentration region.

Similarly, a master curve is obtained (Figure 9.5(b)) when the structure factor, $S_{cc}(0)$ of HASE-20-80-2 at various ionic strength and particle concentrations was plotted against the effective volume fraction, ϕ_{eff} calculated from Equation (7.3).

Figure 9.5 Structure factor, $S_{cc}(0)$ of HASE-20-80-2 at $\alpha=1$ and three different salt concentrations, mM KCl as a function of (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{\text{eff}} = k c$. The solid lines are to guide the eye, which shows the reducing trend of $S_{cc}(0)$ as the salt concentrations vary.

9.4 SUMMARY

It has been demonstrated that a simple turbidimetric analysis of a microgel suspension is capable of furnishing structural information in the region of low scattering angles. In particular, the structure factor at zero scattering angle can be determined with good precision. The structure factor, $S_{cc}(0)$ of microgels at various cross-linked densities and ionic strength seemed to fall onto a single master-curve when plotted against the effective volume fraction, $\phi_{\text{eff}} = kc$, which clearly suggest that particle interaction potential and osmotic compressibility is a function of effective volume fraction of microgels. Thus, turbidimetry provides additional and useful information on particle interaction in a regime of concentration, which is difficult to access by other methods.

10 DYNAMICS AND MICROSTRUCTURE OF CORE-SHELL MICROGEL PARTICLES

In this chapter, the validity and limitation of the proposed semi-empirical approach to model charged soft microgel particles on a different soft sphere system are examined. The studies were expanded to core-shell pH-responsive microgels consisting of PMMA particles grafted with a soft layer of methacrylic acid-ethyl acrylate (MAA-EA) cross-linked with di-allyl phthalate (DAP) and the schematic representation is illustrated in Figure 10.1, at both unneutralized and fully neutralized state.

Figure 10.1 Schematic representation of the core-shell pH-responsive microgel particles at different state, (a) unneutralized ($\alpha = 0$) and (b) fully neutralized ($\alpha = 1$). The black core represents the PMMA particle and the full dots between chain segments in the shell represent the cross-linker. The counter-ions from the base (NaOH) used to neutralize the microgels are represented by the symbol Na^+ and the symbol $\ominus$ represents the neutralized carboxylic groups, COO^- . The outer shell represents the region where electro-neutrality is not satisfied locally.

Two different model core-shell pH-responsive microgel systems were studied; i.e. (a) CS-20-80-2 and (b) CS-50-50-1 and the particle descriptions are given in Table 3.1(b). Similarly, we manipulate the characteristics of microgel particles and their corresponding interaction potential by varying the followings; (a) degree of neutralization of MAA groups, α , (b) salt concentrations, and (c) molar ratio of acidic units (MAA).

10.1 PARTICLE SIZE CHARACTERIZATION

10.1.1 DYNAMIC LIGHT SCATTERING MEASUREMENTS

The pH-responsive core-shell microgel particles containing 20 mole percent MAA (CS-20-80-2) and 50 mole percent MAA (CS-50-50-1) grafted to the PMMA core were characterized in dilute solution using the Brookhaven dynamic light scattering (DLS) system for α ranging from 0 to 1.0 and in salt concentration ranging from 0.1 to 100 mM KCl. In the unneutralized state, the particles exhibit a microstructure close to that of a model hard sphere with a hydrodynamic radius, R_h of ~ 100 nm.

In Figure 10.2, the thickness of the surface layer containing the pH-responsive network (MAA-EA) for both CS-20-80-2 and CS-50-50-1 was plotted against α for varying [KCl] concentrations. This shell thickness was derived from the hydrodynamic radius ($R_h - R_c$), where R_c is the radius of the core (PMMA) particles with a value of ~ 84 nm also measured using the Brookhaven dynamic light scattering system. The pH-dependent ($R_h - R_c$) for both CS-20-80-2 and CS-50-50-1 show a

continuous increase as α increases from 0 to 1.0, representing the steady expansion of the shell due to enhanced osmotic pressure exerted by the counter-ions trapped within the shell of the polymeric network by the electrostatic attraction exerted from the charged carboxylate groups as depicted in Figures 10.1 and 10.2. As anticipated, microgels with higher amounts of charged carboxylate groups (CS-50-50-1) exhibit a larger swelling behavior. The maximum ($R_h - R_c$) for CS-50-50-1 is ~ 240 nm, compared to ~ 120 nm for CS-20-80-2.

Swelling is reduced when the salt concentration, [KCl] increases as depicted in Figure 10.2. When [KCl] increases from 0.1 to 100 mM, ($R_h - R_c$) may decrease by nearly 50%, i.e., from ~ 120 to ~ 60 nm for CS-20-80-2, which is attributed to the charge shielding effect of counter-ions (salt) on the negatively charged carboxylate groups, thus reducing the osmotic pressure inside the corona shell.

Figure 10.2 (a) Dependence of shell thickness, $R_h - R_c$ on α for core-shell microgels with different mole percent MAA, (a) CS-20-80-2 and (b) CS-50-50-1, in different salt concentrations (mM KCl); (Δ : 0.1 mM; $\circ$: 10 mM; $\square$: 100 mM).

It is evident from Figures 10.2(a) and (b) that a similar trend is observed where the particle size begins to increase at a faster rate as reflected by the sharp increase at $\alpha > 0.3$, which further points to a transition region reflecting the conformational change of microgel particles during the neutralization process, as discussed earlier.

10.1.2 STATIC LIGHT SCATTERING MEASUREMENTS

The microgel solutions were further investigated by static light scattering experiments. This allows the apparent radius of gyration, $R_{g,app}$, to be determined. The dimensionless ratio R_g/R_h has characteristic values for different polymer architectures, for hard spheres $R_g/R_h = 0.778$ and for microgels R_g/R_h is usually smaller than the hard sphere value [Nerger, 1979; Burchard, 1989]. The ratio R_g/R_h of the core-shell microgels are shown in Figure 10.3, and in the unneutralized state, the ratio is in the range of the hard sphere value, when the particles is in a collapsed state.

With increasing α , R_g/R_h decreases where microgels with higher MAA content and lower salt concentrations experience larger drop. R_g is sensitive to the refractive index distribution (mass distribution) within the microgel, while R_h is sensitive to hydrodynamics. The deviation of R_g/R_h from the hard sphere value at high α , suggests that the particles are significantly swollen and the network density decreases at the particle surface because the core is covered with dangling chains that increase the hydrodynamic radius, R_h which have a smaller effect on the radius of gyration, R_g and hence, the ratio R_g/R_h decreases.

Figure 10.3 The ratio of R_g/R_h as a function of neutralization degree, α obtained from static and dynamic light scattering for core-shell microgels with different mole percent MAA, (a) CS-20-80-2 and (b) CS-50-50-1, in different salt concentrations (mM KCl); ($\triangle$: 0.1 mM; $\circ$: 10 mM; $\square$: 100 mM).

10.2 RHEOLOGICAL BEHAVIOR

Figures 10.4(a) to 10.4(d) display the flow properties of four different core-shell microgel systems, namely; (a) microgel concentration, c (wt%); (b) neutralization degree (α) of MAA groups; (c) salt concentration [KCl]; and (d) molar ratio of MAA groups. At low particle concentration, c , low α (< 0.5), high salt environment and low content of MAA, the samples display a Newtonian behavior with a low shear viscosity close to that of water. The effective volume, ϕ_{eff} of the microgels in solution is small due to insignificant degree of swelling.

At high particle concentration, ($c > 2\text{wt\%}$), high α (> 0.5), low salt environment and high content of MAA, the enhanced osmotic pressure exerted by the counter-ions trapped inside the polymeric network by the large number of charged carboxylate groups causes an increase in the effective volume, ϕ_{eff} occupied by the particles. Such increase essentially decreases the inter-particle distance, where the interaction forces between the swollen particles increase sharply, resulting in the shear-thinning behavior. The low shear viscosity can change by nearly four orders of magnitude with increasing neutralization degree, for example, CS-50-50-1 at 4 wt% particle concentration at $\alpha = 0$ possesses a low shear viscosity of ~ 0.004 Pa.s and it increases to ~ 40 Pa.s at $\alpha = 1$. The low shear viscosity, η_0 was determined from a regression fit to the Cross model (Equation (4.1)) and are represented by the solid lines in Figure 10.4.

Figure 10.4 Viscosity versus shear rate of model core-shell microgels at four different conditions; (a) varying microgel concentration, c (wt%) of CS-50-50-1; (b) varying neutralization degree (α) of MAA groups of CS-50-50-1; (c) varying salt concentrations (mM KCl) of CS-50-50-1 and (d) varying molar ratio of MAA groups (% MAA). The solid lines denote mathematical fittings according to Equation (4.1).

10.3 SEMI-EMPIRICAL APPROACH TO MODEL CORE-SHELL PARTICLES

The proposed semi-empirical approach to model soft condensed particles as described in Chapter 7 was extended to these core-shell pH-responsive microgels. The specific volume, k is a function of $k = f(c, \alpha, [\text{KCl}], \text{wt\% DAP}, \text{\% MAA})$. Similarly, the values of k were determined from the mathematical fitting of the data to the form of the modified Krieger-Dougherty equation shown in Equation (2.22),

$$\frac{\eta_0}{\eta_s} = \left(1 - \frac{kc}{\phi_m}\right)^{-[\eta]\phi_m}.$$

Figures 10.5(a) to 10.5(d) show the specific volume, k as a function of concentration of particles for three different systems of the core-shell microgels, namely; (a) varying degree of neutralization (α) of MAA groups; (b) varying salt concentration $[\text{KCl}]$; and (c) varying molar ratio of MAA groups. The general trend of specific volume, k can be described by Equation (7.1),

$$\frac{k - k_{\min}}{k_0 - k_{\min}} = \left[1 + \left(\frac{c}{c'}\right)^2\right]^{-m}$$

and the solid lines in Figures 10.5 denote these mathematical fittings. Microgel particles are highly swollen at large α , low salt environment and high content of MAA. Such particles exhibit strong dependence of k on particle concentration, where (k/k_0) may decrease from 1.0 to 0.5.

Figure 10.5 Specific volume, k as a function of concentration of particles for three different core-shell microgel systems namely; (a) CS-50-50-1 at varying degree of neutralization (α) of MAA groups; (b) CS-50-50-1 at varying salt concentrations (mM KCl); and (c) varying molar ratio of MAA groups (% MAA). The solid lines denote mathematical fittings according to Equation (7.1).

Figures 10.6(a) and 10.6(b) summarize the dependence of c' and m on neutralization degree, α at three different salt concentrations (mM KCl) of CS-20-80-2 and CS-50-50-1 core-shell microgels determined from the mathematical fitting of the data to Equation (7.1).

Figure 10.6 (a) c' and (b) m , as a function of α for CS-20-80-2 (open symbols) and CS-50-50-1 (filled symbols) at three different salt concentrations, (mM KCl).

As neutralization degree, α increases and salt concentration reduces, c' decreases and m increases because the enhanced osmotic pressure causes the shell of the particle to swell further, which decreases the inter-particle distance resulting in an increase in the interaction forces between the swollen particles. Thus, the critical concentration, c' at which the soft particle starts to shrink decreases and the rate of shrinkage, m increases.

The effective volume fraction of soft microgel particles at various particle concentrations can be determined from Equation (7.3) by substituting Equation (7.1) into $\phi_{\text{eff}} = k c$. This expression corrects for the changes in the volume fraction of soft particles to that of equivalent hard sphere. Excellent agreement with the K-D model prediction was observed for moderate to high volume fraction where a common curve was obtained when the viscosity data were plotted using the modified ϕ_{eff} determined from Equation (7.3) (Figures 10.7(a) to 10.7(c)). This strongly suggests that the generalized approach is able to capture the physics of soft microgel particles and the form of Equation (7.3) has the capability of predicting the relative viscosity of this core-shell system.

Figure 10.7 Relative viscosity versus ϕ_{eff} of core-shell systems; (a) CS-20-80-2 and (b) CS-50-50-1 at three different α s ; ($\triangle$: $\alpha=0$; $\circ$: $\alpha=0.5$; $\square$: $\alpha=1.0$) and three different salt concentrations, [KCl] ; no salt (open), 10 mM (grey) and 100 mM (black). Solid line denotes the K-D model (Equation (2.3)).

10.4 THEORETICAL APPROACH TO MODEL CORE-SHELL PARTICLES

The viscosity data of our pH-responsive core-shell particles in salt free solutions (Figures 10.7(a) and (b)) were replotted in Figure 10.8 using the effective volume fraction, ϕ_{eff} computed from Equation (2.27) and $\tilde{Q}$ determined from Equation (2.26).

As discussed in Chapter 8, a more accurate method to determine Γ is to measure the concentration of free counter-ions as a function of microgel concentration using the sodium (Na^+) ion selective electrode. Within the experimental accuracy, the data agrees well with the K-D model (Equation (2.3)) for dilute to high volume fraction of core-shell particles.

Figure 10.8 Relative low shear viscosity versus effective volume fraction, ϕ_{eff} of core shell particles with varying MAA content in salt free solutions; (a) CS-20-80-2 and (b) CS-50-50-1 at two different α s ($\triangle$: $\alpha=0.5$; $\circ$: $\alpha=1.0$). ϕ_{eff} was calculated from Equation (2.27) where Γ was measured using Na^+ ISE and the solid line denotes the hard sphere behavior according to Equation (2.3).

Figure 10.9 shows a comparison of ϕ_{eff} determined using the semi-empirical approach (open symbols) proposed by our group (Equation (7.3)) with the theoretical approach (closed symbols) proposed by Cloitre and co-workers (Equation (2.27)) for two core-shell systems, CS-20-80-2 and CS-50-50-1. The ϕ_{eff} determined from these two methods are in good agreement, and strongly suggests that the semi-empirical approach is valid in capturing the physics of soft core-shell particles and the form of (Equation (7.3)) has the capability of predicting the relative viscosity of different systems.

Figure 10.9 Comparison of values of ϕ_{eff} determined using the semi-empirical approach (Equation (7.3)) (open symbols) with the theoretical approach (Equation (2.27)) where values of Γ was measured using Na^+ ISE (filled symbols) of core-shell systems in salt free solutions; (a) CS-20-80-2 and (b) CS-50-50-1 at two different α s (Δ : $\alpha=0.5$; $\circ$: $\alpha=1.0$).

10.5 STRUCTURE FACTORS FROM TURBIDITY

The method of Ballauff and co-workers described in Section 2.7.1 was employed to extract the particle osmotic compressibility contribution to the structure factor from the turbidity data of the core-shell system. Figure 10.10(a) display a plot of specific turbidity, τ/c as a function of c at fixed wavelength, λ of CS-50-50-1 at $\alpha=1$, where $Z(\lambda^2, c)$ can be calculated from Equation (2.42). A plot of $Z(\lambda^2, c)$ as a function of $1/\lambda^2$ is then given in Figure 10.10(b), and the intercept of this plot at each concentration is the structure factor $S(0)$ (Equation (2.40)).

Figure 10.10 (a) Specific turbidity, τ/c as a function of microgel concentration, c at fixed wavelength, λ and (b) integrated structure factor, $Z(\lambda^2, c)$ as a function of $1/\lambda^2$ at different microgel concentration, c of CS-50-50-1 in salt free solution and $\alpha = 1$. The solid lines are the linear curve fits to the data to extract the intercept.

10.5.1 STRUCTURE FACTORS AS A FUNCTION OF NEUTRALIZATION DEGREE AND IONIC STRENGTH

Figures 10.11 and 10.12 display a plot of $S_{cc}(0)$ of core-shell microgels, CS-50-50-1 as a function of microgel concentration at different degree of neutralization, α (Figure 10.11(a)) and in different salt concentrations (Figure 10.12(a)). In the dilute solution regime ($c < 0.1\text{wt}\%$), inter-particle interaction is absent and the osmotic compressibility, $S_{cc}(0)$ is fairly similar for microgels with different α s and salt concentrations (mM KCl).

Figure 10.11 Osmotic compressibility, $S_{cc}(0)$ of core-shell microgels, CS-50-50-1 in salt free solutions at varying degree of neutralization, α as a function of, (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{\text{eff}} = k c$. The solid lines are to guide the eye, which shows the reducing trend of $S_{cc}(0)$ as α vary.

With increasing microgel concentration, the inter-particle distance between microgels is reduced, thus increasing the dispersion resistance to particle compression, which results in a corresponding decrease in osmotic compressibility, $S_{cc}(0)$. Microgels are highly swollen at large α and low salt environment, where the effective volume fraction, ϕ_{eff} occupied by these particles increases. Such increase essentially decreases the inter-particle distance and the interaction forces between the swollen particles increase sharply, resulting in a larger decrease in $S_{cc}(0)$ where $S_{cc}(0)$ may decrease from 1.0 to 0.35 for CS-50-50-1 at $\alpha = 1$ and 0.1 mM KCl solutions as seen in Figures 10.11 and 10.12.

Figure 10.12 Osmotic compressibility, $S_{cc}(0)$ of fully neutralized ($\alpha=1$) core-shell microgels, CS-50-50-1 at varying salt concentrations (mM KCl) as a function of, (a) microgel concentration (g/ml) and (b) effective volume fraction, $\phi_{eff} = k c$. The solid lines are to guide the eye, which shows the reducing trend of $S_{cc}(0)$ as [KCl] vary.

Similarly, the osmotic compressibility, $S_{cc}(0)$ of core-shell microgels, CS-50-50-1 at various microgel concentration, degree of neutralization, α and different salt concentrations was plotted against the effective volume fraction, ϕ_{eff} calculated from Equation (7.3),

$$\phi_{eff} = k_{min} + (k_0 - k_{min}) \left[1 + \left(\frac{c}{c_0} \right)^2 \right]^{-m} * c ,$$

when Equation (7.1) was substituted into $\phi_{eff} = kc$ as shown in Figures 10.11(b) and 10.12(b). All the data determined at different α and salt concentrations seemed to fall onto a single master-curve, which clearly suggest that particle interaction potential and osmotic compressibility is a function of effective volume fraction of microgels.

10.6 SUMMARY

The utility of the new semi-empirical approach was tested against two different core-shell pH-responsive microgel systems and excellent agreement was obtained. In addition, good agreement was observed when our new semi-empirical approach was compared against a theoretical model, which confirmed the validity of the proposed semi-empirical approach to model charged soft microgel particles.

11 CONCLUSIONS

The characteristics of model pH-responsive nano-colloidal systems consisting of methacrylic acid-ethyl acrylate (MAA-EA) cross-linked with di-allyl phthalate (DAP) and their corresponding interaction potential was manipulated by varying the following; (a) degree of neutralization of MAA groups, α , (b) salt concentrations, (c) microgel cross-linked density, and (d) molar ratio of MAA-EA. Neutralization of acid groups increases the osmotic pressure exerted by counter-ions trapped in the polymeric network against the ions in bulk solution, which is responsible for the swelling and increase in viscosity.

In Chapter 4, the most striking feature observed is that the viscosity exhibits a maximum at ~ 1 wt% DAP and the viscosity decreases to a steady value at 4 wt% DAP, which is independent of pH and particle concentrations for microgels with 20 mole percent MAA. Static light scattering results confirmed this optimum density as the critical point where sufficient cross-linked points are present to produce permanent junctions that permit optimal swelling of the nano-colloidal particles. Comparison with the theoretical scaling law $Q \propto (\alpha N_x)^{3/2}$ indicates that the swelling ratio at maximum swelling Q_m ($\alpha=1$) does not scale with $N_x^{3/2}$ for cross-linked density lower than 1 wt%. This confirmed that there is substantial expulsion of polymer chains from the particles during neutralization which causes the maximum swelling ratio Q_m to be lower than theoretical prediction.

In Chapter 5 and 6 it was demonstrated that at high microgel concentrations, high MAA content and low salt environment, the swollen MAA-EA microgel possesses strong electrostatic repulsion that imparts significant viscoelasticity. The plateau modulus G_p increases with concentration and α and a master-curve was obtained when G_p was plotted against ϕ_{eff} . This is a clear evidence that G_p is a function of the effective volume fraction and the effect of pH-dependent swelling on the modulus is minimized when the ϕ_{eff} was used as the concentration variable.

The theoretical scaling law, $Q \propto (y\alpha N_x)^{3/2}$ was successfully expanded to include new data containing microgel systems with varying salt concentrations [KCl] as described in Chapter 6. Excellent agreement was obtained where all the data fall on a master curve, and this confirmed that the new scaling law, $\frac{N_x}{c_0} (C_{K^+} + C_{Na^+}) Q + Q^{2/3} \propto y N_x \alpha$, is capable of predicting the relative swelling ratio of microgel systems with varying cross-linked densities, N_x , molar fraction of acidic units, y , neutralization degree, α and different salt environment, C_{K^+} .

These significant findings have contributed to the development of a unified semi-empirical approach for predicting the viscosity of dilute and concentrated hard and soft sphere systems. We demonstrated that the classical approach where specific volume, k is a constant determined at dilute solution regime, could not account for the prevailing physics at higher volume fraction. Instead, we introduced a variable specific volume, k to convert the mass concentration to effective volume fraction. With increasing particle concentration, the concentration of free counter-ions in the

solution can be large enough to induce an osmotic de-swelling of soft particles, resulting in the particle shrinkage. The viscosity data for a wide variety of cross-linked microgel systems as well as core-shell pH-responsive microgels at different neutralization degree showed excellent agreement with the modified Krieger-Dougherty model as discussed in Chapters 7 and 10 respectively.

In addition, the validity of this new semi-empirical approach was confirmed by comparing against the theoretical model for determining the effective volume

fraction, $\phi = \frac{\tilde{Q}}{V_m c_0} \frac{\rho_s}{\rho_p} c$ whereby excellent agreement was observed for a wide variety

of microgel systems as shown in Chapters 8 and 10. This present approach is extremely valuable to scientists and technologists working with soft particles as the flow properties of these interesting systems can be predicted *a priori*.

Finally, as a supplement, it was demonstrated that a simple turbidimetric analysis of these model pH-responsive nano-colloidal systems is capable of furnishing the structure factor, which is a direct indication of particle interaction in a regime of concentration which is difficult to access by other methods. The osmotic compressibility, $S_{cc}(0)$ of microgels at various cross-linked densities and ionic strength seemed to fall onto a single master-curve when plotted against the effective volume fraction, $\phi_{eff} = k c$, which clearly suggest that particle interaction potential and osmotic compressibility is a function of effective volume fraction of microgels.

12 RECOMMENDATIONS FOR FUTURE WORK

The significant breakthrough demonstrated in the current study is the development of a new unified semi-empirical approach to predict the viscosity of dilute and concentrated hard and soft sphere systems. Experimental results were obtained, which confirmed the validity of this approach on a wide variety of cross-linked microgel systems as well as core-shell pH-responsive microgels. With these findings, it is interesting to extend our investigation to other varieties of soft sphere systems, such as thermal-responsive microgels, which may help to further strengthen the validity of this new approach. Further analysis on the physical meaning of the parameters in the semi-empirical model (Equation (7.1)) is also in progress.

Previous studies have shown that the theoretical scaling law, $Q \propto (y\alpha N_x)^{3/2}$ is capable of predicting the relative swelling of polyelectrolyte microgels in salt free solutions. In addition, utilizing the swelling ratio at finite concentration, $\tilde{Q}$, as a function of the swelling ratio at infinite dilution Q , the mass concentration of a salt free dispersion can be converted to effective volume fraction through a simple

theoretical relation, $\phi = \frac{\tilde{Q}}{V_m c_0} \frac{\rho_s}{\rho_p} c$. We successfully expanded the theoretical scaling

law, to include new data containing microgel systems with varying salt concentrations

given as $\frac{N_x}{c_0} (C_{K^+} + C_{Na^+}) Q + Q^{2/3} \propto y N_x \alpha$. Coupling this with careful

electromotive measurements at varying microgel concentration and salt content, the

swelling ratio at finite concentration as well as the relationship between mass concentration and volume fraction can be expanded to include varying ionic strength conditions.

Another area that should be pursued is the application of stimuli responsive nano-colloidal particles as materials for drug and protein delivery vehicles. We plan to synthesize pH and temperature responsive soft microgels, which are biocompatible in nature. Our current knowledge in predicting the swelling ratio of soft microgels upon changing external conditions will provide important insights and could form an important basis for examining the rate of loading and release of drugs and proteins within these biocompatible systems.

REFERENCES

- Ackerson, B.J. and Pusey, P.N. (1988). Shear induced order in suspensions of hard spheres. **Phys. Rev. Lett.** 61, 1033-1036.
- Antonietti, M., Bremser, W. and Schmidt, M. (1990). Micro-emulsion polymerization to synthesize spherical microgels. **Macromolecules**. 23, 3796-3805.
- Apfel, U., Grunder, R. and Ballauff, M. (1994). A turbidity study of particle interaction in latex suspensions. **Colloid Polym Sci.** 272, 820-829.
- Apfel, U., Horner, K.D. and Ballauff, M. (1995). Precise analysis of the turbidity spectra of a concentrated latex. **Langmuir**. 11, 3401-3407.
- Baker, W.O. (1949). Microgels-New molecules and emulsion copolymerization. **Ind. Eng Chem.** 4, 511-524.
- Ballauff, M. (2003). Nanoscopic Polymer Particles with a well-defined surface: synthesis, characterization and properties. **Macromol. Chem. Phys.** 204, 220-234.
- Bartsch, E., Frenz, V., Baschnagel, J., Scharfel, W. and Sillescu, H. (1997). The glass transition dynamics of polymer micronetwork colloids. A mode coupling analysis. **J. Chem. Phys.** 106 (9), 3743-3756.
- Batchelor, G.K., (1976). Brownian diffusion of particles with hydrodynamic interaction. **J. Fluid Mech.** 74, 1-29.
- Bergenholtz, J., Willenbacher, N., Wagner, N.J. and Mellema, J. (1998). Colloidal charge determination in concentrated liquid dispersions using torsional resonance oscillation. **J. Colloid Interface Sci.** 202 (2), 430-440.

- Bolle, T. (1993). Microemulsion polymerization of 1,4-divinylbenzene and styrene. **Thesis, University of Stuttgart.**
- Borrega, R., Cloitre, M., Betremieux, I., Ernst, B. and Leibler, L. (1999). Concentration dependence of the low-shear viscosity of polyelectrolyte micro-networks: From hard spheres to soft microgels. **Europhys. Lett.** 47 (6), 729-735.
- Bossis, G. and Brady, J.F. (1989). The rheology of Brownian suspensions. **J. Chem. Phys.** 91, 1866-1879.
- Brandrup, J. and Immergut, E.H. (1989). **Polymer Handbook.** 3rd ed. John Wiley.
- Brenner, H. (1974). In **Progress in Heat and Mass Transfer.** 2nd ed., edited by W. R. Schowalter, Pergamon, New York. Chapter 1, 195-204.
- Brown, W. (1993). **Dynamic Light Scattering – the Method and Some Applications.** Clarendon Press, Boston.
- Burchard, W., Richtering, W. (1989). **Progress Colloid Polymer Science.** 80, 151-160.
- Chu, B. (1991). **Laser Light Scattering – Basic Principles and Practice.** 2nd Ed. Academic Press, Boston.
- Cloitre, M., Borrega, R., Monti, F., Leibler, L. (2003). Structure and flow of polyelectrolyte microgels : from suspensions to glasses. **C.R. Physique.** 4, 221-230.
- Einstein, A. (1906). Eine neue Bestimmung der Moleküldimension. **Ann. Phys.** 19, 289-306.

- Einstein, A. (1911). Berichtigung zu meiner Arbeit; Eine neue Bestimmung der Moleküldimensionen. **Ann. Phys.** 34, 591-592.
- Funke, W.E., Okay, O., and Joos-Muller, B. (1998). Microgels-Intramolecularly Cross-linked Macromolecules with a Globular structure. **Advances in Polymer Science.** 136, 140-234.
- Goddard, J.D. (1978). Tensile Behavior of Power-Law Fluids Containing Oriented Slender Fibers. **J. Rheology.** 22 (6), 615-622.
- Guo, L. (1997). **M. Eng. Thesis.** Rheology of alkali-soluble associative polymer in aqueous solution. Singapore. Nanyang Technological University.
- Guo, L., Tam, K.C. and Jenkins, R.D. (1998). Effects of salt on the intrinsic viscosity of model alkali-soluble associative polymers. **Macromol. Chem. Phys.** 199, 1175-1184.
- Horn, F.M., Richtering, W., Bergenholtz, J., Willenbacher, N. and Wagner, N.J. (2000). Hydrodynamic and colloidal interactions in concentrated charge-stabilized polymer dispersions. **J. Colloid Interface Sci.** 225, 166-178.
- Horner, K.D., Topper, M. and Ballauff, M. (1997). Assessment of the depletion forces in mixture of a polystyrene latex and hydroxyethyl cellulose by turbidimetry. **Langmuir.** 13, 551-558.
- Huggins, M.L. (1942). The Viscosity of Dilute Solutions of Long-Chain Molecules. IV. Dependence on Concentration. **J Am Chem Soc.** 64, 2716-2718.
- Hunter, R.J. (1991). **Foundations of Colloid Science**, Vol. 1. Clarendon Press, Oxford.
- Hunter, R.J. (1991). **Foundations of Colloid Science**, Vol. 2. Clarendon Press, Oxford.

Kerker, M. (1969). **The scattering of light and other electromagnetic radiation.** Academic Press, New York. p 427.

Kjoniksen, A.L., Nystrom, B., Iversen, C., Nakken, T., Palmgren, O. and Tande, T. (1997). Viscosity of Dilute Aqueous Solutions of Hydrophobically Modified Chitosan and Its Unmodified Analogue at Different Conditions of Salt and Surfactant Concentrations. **Langmuir**. 13 (19), 4948-4952.

Koppel, D.E. (1972). Analysis of Macromolecular Polydispersity in Intensity Correlation Spectroscopy: The Method of Cumulants. **J. Chem. Phys.** 57(11), 4814-4820.

Krieger, I.M. (1972). Rheology of Monodispersed Lattices. **Adv. Colloid Interface Sci.** 3, 111-136.

Krieger, I.M. and Eguiluz, M. (1976). The second electroviscous effect in polymer lattices. **Trans. Soc. Rheol.** 20, 29-45.

Kumacheva, E., Rharbi, Y., Winnik, M.A., Guo, L., Tam, K.C. and Jenkins, R.D. (1997). Fluorescence studies of an alkaline swellable associative polymer in aqueous solution. **Langmuir**. 13, 182-186.

Larson, R.G. (1999). **The structure and rheology of complex fluids.** New York: Oxford University Press. Chapter 1, 3-18, and Chapter 10, 426-458.

Lionberger, R.A. and Russel, W.B. (1994). High frequency modulus of hard sphere colloids. **J. Rheol.** 38, 1885-1908.

Magny, B., Iliopoulos, I., Audebert, R., Dubin, P., Bock, J., Davis, R., Schulz, D.N. and Thies, C. (1996). **Macromolecular complexes in chemistry and biology.** Berlin. Springer. p. 51-62.

- Meeker, S.P., Poon, W.C.K. and Pusey, P.N. (1997). Concentration dependence of the low-shear viscosity of suspensions of hard-sphere colloids. **Phys. Rev. E.** 55, 5718-5722.
- Metzner, A.B. (1985). Rheology of suspensions in polymeric liquids. **J. Rheol.** 29, 739-775.
- Muroi, S. (1967). Some physicochemical properties of poly(ethyl acrylate) emulsions containing carboxyl groups. **J. Applied Polym. Sci.** 10, 713-729.
- Napper, D.H. (1983). **Polymeric stabilization of colloidal dispersions**. London Academic Press.
- Ng, W.K., Tam, K.C., and Jenkins, R.D. (1999). Evaluation of intrinsic viscosity measurements of hydrophobically modified polyelectrolyte solutions. **Eur Polym J.** 35(7), 1245-1252.
- Onoda, G.Y. and Liniger, E.R. (1990). Random loose packings of uniform spheres and the dilatancy onset. **Phys. Rev. Lett.** 64(22), 2727-2730.
- Ottewill, R.H. and Richardson, R.A. (1982). Characterization of particle morphology by scattering techniques. **Colloid Polym. Sci.** 260, 708-715.
- Paulin, S.E., Ackerson, B.J. and Wolfe, M.S. (1996). Equilibrium and Shear Induced Nonequilibrium Phase Behavior of PMMA Microgel Spheres. **J. Colloid Interface Sci.** 178, 251-262.
- Phung, T.N., Brady, J.F. and Bossis, G. (1996). Stokesian dynamics simulation of Brownian suspensions. **J. Fluid Mech.** 313, 181-207.
- Pipkin, A.C. (1992). **Lectures on Viscoelasticity Theory**. Springer-Verlag, New York.

- Quadrat, O., Mrkvickova, L., Jasna, E. and Snupareck, J. (1990). Rheological Studies of Aqueous Dispersions of Carboxylic Acid Latices. **J. Colloid Polym. Sci.** 268, 493-501.
- Riddle, M.J. (1977). **Rheology Research Center Report** No. 47, University of Wisconsin.
- Rodriguez, B.E. and Wolfe, M.S. (1994). Nonuniform Swelling of alkali Swellable Microgels. **Macromolecules.** 27, 6642-6647.
- Russel, W.B. (1980). Review of the role of colloidal forces in the rheology of suspensions. **J. Rheol.** 24 (3), 287-317.
- Russel, W.B. (1984). The Huggins coefficient as a means for characterizing suspended particles. **J. Chem. Soc. Faraday Trans. 2** (80), 31-41.
- Russel, W.B., Saville, D.A, and Schowalter, W.R. (1989). **Colloidal Dispersions.** Cambridge University, Cambridge.
- Saunders, B.R., Vincent, B. (1999). Microgel particles as model colloids: theory, properties and applications. **Adv. In Colloid Interface Sci.** 80, 1-25.
- Saunders, B.R., Crowther, H.M. and Vincent, B. (1997). Poly[(methyl methacrylate)-co-(methacrylic acid)] microgel particles: swelling control using pH, cononsolvency, and osmotic deswelling. **Macromolecules.** 30, 482-487.
- Schulman, J.H., Stockennius, W. and Prince, L.M. (1959). Microemulsions as medium for preparing microgels. **J. Phys. Chem.** 63, 1677-1690.
- Senff, H. and Richtering, W. (1999). Temperature sensitive microgel suspensions: colloidal phase behavior and rheology of soft spheres. **J. Chem. Phys.** 111 (4), 1705-1711.

- Senff, H. and Richtering, W. (1999). Rheology of a temperature sensitive core-shell latex. **Langmuir**. 111 (4), 1705-1711.
- Senff, H. and Richtering, W. (2000). Influence of cross-linked density on rheological properties of temperature-sensitive microgel suspensions. **J. Colloid Polym. Sci.** 278, 830-840.
- Shashoua, V.A. and Beaman, R.G. (1958). Preparation of microgels by emulsion copolymerization (ECP). **J. Polym. Sci.** 33, 101-124.
- Shay, G.D. (1989). **Polymers in Aqueous Media; Glass**, J.E., Ed.; American Chemical Society: Washington, DC.
- Shikata, T. and Pearson, D.S. (1994). Viscoelastic behavior of concentrated spherical suspensions. **J. Rheol.** 38 (3), 601-615.
- Van der Werff, J.C. and De Kruif, C.G. (1989). Hard-sphere colloidal dispersions: the scaling of rheological properties with particle size, volume fraction and shear rate. **J. Rheol.** 33 (3), 421-454.
- Van Der Werff, J.C., De Kruif, C.G., Blom, C. and Mellema, J. (1989). Linear viscoelastic behavior of dense hard-sphere dispersions. **Phys. Rev. A**. 39, 795-807.
- Verbrugge, C.J. (1970). Mechanism of alkali thickening of acid-containing emulsion polymers. I. Examination of latexes by means of viscosity. **J. Appl Polym. Sci.** 14 (4), 897-909.
- Verwey, E.J., and Overbeek, J.T.G. (1948). **Theory of stability of lyophobic colloids**. Elsevier, Amsterdam.
- Volpert, E., Selb, J. and Candau, F. (1996). Influence of the Hydrophobe Structure on Composition, Microstructure, and Rheology in Associating

Polyacrylamides Prepared by Micellar Copolymerization. **Macromolecules**. 29, 1452-1463.

Volpert, E., Selb, J. and Candau, F. (1998). Associating behaviour of polyacrylamides hydrophobically modified with dihexylacrylamide **Polymer**. 39 (5), 1025-1033.

Wang, C., Tam, K.C., Jenkins, R.D. and Bassett, D.R. (2000). Potentiometric titration and dynamic light scattering of hydrophobically modified alkali soluble emulsion (HASE) polymer solutions. **Phys. Chem. Chem. Phys.** 2 (9), 1967-1972.

Wagner, N.J. (1993). Optical measurement of the contributions of colloidal forces to the rheology of concentrated suspensions. **J. Colloid Interface Sci.** 161, 169-173.

Weiss, A., Dingenouts, N. and Ballauff, M. (1998). Comparison of the effective radius of sterically stabilized latex particles determined by small-angle X-ray scattering and by zero shear viscosity. **Langmuir**. 14, 5083-5087.

Willey, S.J. and Macosko, C.W. (1978). Steady shear rheological behavior of PVC plastisols. **J. Rheol.** 22 (5), 525-545.

Wolfe, M.S., and Scopazzi, C. (1989). Influence of cross-linking density on microgel interaction. **J. Colloid Interface Sci.** 133, 265-282.

APPENDIX A

Summary of hydrodynamic radius, R_h and the fitted parameters, c' and m obtained by fitting Equation (7.1) onto experimental data of the various microgel systems studied

α	R_h (nm)	c' (g/ml)	m
HASE-20-80-1 at 0.1 mM KCl			
0.0	36.3	0.030	0.042
0.5	107.0	0.017	0.260
0.8	132.2	0.012	0.425
1.0	145.7	0.008	0.452
HASE-20-80-2 at 0.1 mM KCl			
0.0	40.5	0.031	0.035
0.5	96.0	0.020	0.180
0.8	112.8	0.014	0.300
1.0	116.0	0.010	0.335
HASE-20-80-2 at 1 mM KCl			
0.0	38.7	0.032	0.035
0.5	83.2	0.023	0.145
0.8	98.2	0.017	0.262
1.0	103.3	0.012	0.295
HASE-20-80-2 at 10 mM KCl			
0.0	37.5	0.032	0.035
0.5	75.0	0.024	0.125
0.8	87.5	0.019	0.230
1.0	90.5	0.014	0.250
HASE-20-80-2 at 100 mM KCl			
0.0	32.5	0.032	0.035
0.5	45.0	0.026	0.110
0.8	52.0	0.021	0.200
1.0	57.0	0.017	0.230
HASE-20-80-3 at 0.1 mM KCl			
0.0	41.7	0.032	0.030
0.5	72.8	0.021	0.142
0.8	90.3	0.015	0.274
1.0	96.4	0.012	0.305

HASE-20-80-4 at 0.1 mM KCl			
0.0	41.2	0.033	0.020
0.5	67.9	0.023	0.118
0.8	81.6	0.016	0.237
1.0	87.8	0.014	0.283
α	R_h (nm)	c' (g/ml)	m
HASE-30-70-4 at 0.1 mM KCl			
0.0	45.8	0.028	0.030
0.5	88.0	0.020	0.154
0.8	106.7	0.015	0.294
1.0	116.7	0.013	0.343
HASE-40-60-4 at 0.1 mM KCl			
0.0	49.3	0.025	0.041
0.5	108.2	0.016	0.182
0.8	130.5	0.012	0.323
1.0	142.4	0.009	0.366
HASE-50-50-4 at 0.1 mM KCl			
0.0	53.7	0.023	0.059
0.5	126.5	0.012	0.205
0.8	155.4	0.010	0.359
1.0	169.8	0.007	0.385
CS-20-80-2 at 0.1 mM KCl			
0.0	102.7	0.028	0.022
0.5	158.0	0.025	0.120
0.8	189.6	0.022	0.172
1.0	203.7	0.020	0.200
CS-50-50-1 at 0.1 mM KCl			
0.0	96.4	0.024	0.030
0.5	287.1	0.019	0.180
0.8	308.8	0.016	0.235
1.0	327.7	0.014	0.265

APPENDIX B

Cross model (Equation (4.1)) parameters of the various microgel systems studied

α	κ	m	η_0 (Pa.s)
5 wt% concentration of HASE-20-80-1 at 0.1 mM KCl			
0.5	0.068	0.168	3.83×10^{-2}
0.8	0.611	0.386	8.44×10^{-1}
1.0	1.146	0.502	1.17×10^1
5 wt% concentration of HASE-20-80-2 at 0.1 mM KCl			
0.5	0.023	0.075	1.70×10^{-2}
0.8	0.128	0.273	1.36×10^{-1}
1.0	0.500	0.464	4.93×10^{-1}
5 wt% concentration of HASE-30-70-4 at 0.1 mM KCl			
0.5	0.056	0.116	2.75×10^{-2}
0.8	2.265	0.639	6.32×10^0
1.0	90.00	0.928	1.64×10^3
4 wt% concentration of HASE-40-60-4 at 0.1 mM KCl			
0.5	1.587	0.584	1.07×10^0
0.8	450.0	0.928	1.24×10^3
1.0	1500	1.187	7.68×10^4
4 wt% concentration of HASE-50-50-4 at 0.1 mM KCl			
0.5	105.0	0.848	1.35×10^2
0.8	3000	1.117	1.58×10^4
1.0	8500	1.251	2.50×10^6
5 wt% concentration of CS-50-50-1 at 0.1 mM KCl			
0.5	10.40	0.314	7.85×10^{-2}
0.8	36.20	0.500	7.10×10^0
1.0	122.0	0.625	3.62×10^1