

CHAPTER IV
PART I : CHARACTERISATION OF CATIONIC GUAR/SLES
AGGREGATES

4.1 Introduction

This part is dedicated to studies that were conducted to characterise the SLES/cationic guar system. The primary objective of this part of the study was to identify several points on the SLES/cationic guar phase diagram which produced flocs or aggregates with substantially different physio-chemical properties. The final part of this chapter will then examine the effect of these properties on the ability of the flocs to mediate the frictional properties of hair.

In this part we will first characterise the cationic guar/SLES system, principally through the use of two techniques: surface tension measurement and visual inspection of a range of mixtures in order to identify the phase behaviour and phase boundaries.

Secondly, the dispersed flocs generated at various points in the phase diagram will be characterised by two major techniques including particle sizing techniques and particle mobility measurements.

Thirdly, we will examine a range of different techniques to characterise the isolated, dried flocs. These include microscopy (SEM), measuring the amount of dried floc, FTIR and chemical analysis of the dried flocs.

Finally, we shall examine the inter-relationships between some of these physical properties.

4.2 Characterisation of the Cationic Guar/SLES system

4.2.1 Surface Tension Measurements

4.2.1.1 *Pure Surfactant*

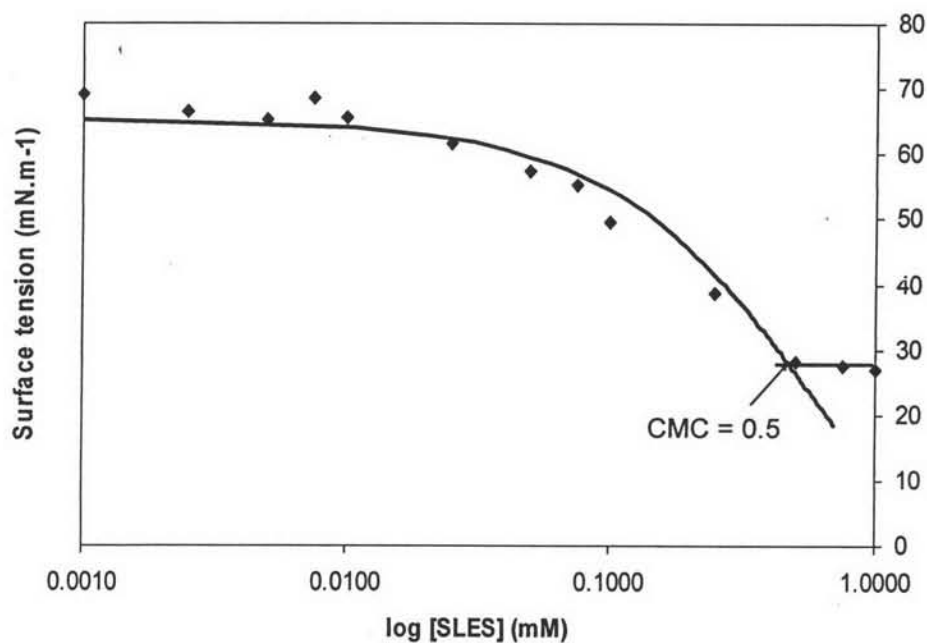


Figure 4.1 Surface tension measurements of an SLES solution at 30 ± 1 °C.

Figure 4.1 shows the surface tension profile of a solution of surfactant (SLES) as a function of the SLES concentration, at a concentration of up to 1 mMol. The above diagram is characteristic of surfactant behaviour. The graph can be divided into three distinct regions. At very low surfactant concentrations the surface tension is approximately constant, but decreases slowly. In this region the surfactant adsorbs at the air/water interface, but has very limited effect in terms of reducing the surface tension due to low concentration and poor packing at the interface. At intermediate surfactant concentrations the surface tension decreases rapidly. In this area the additional surfactant continues to be adsorbed at the air/water interface resulting in a higher concentration at the interface leading to better packing and hence more effective surface tension reduction. At high surfactant concentrations the surface tension is constant and is almost independent of surfactant concentration. In this region, the air/water interface has now become saturated, hence no further

reduction in surface tension becomes possible. Additional surfactant is absorbed into the body of water and aggregates into micelles in order to reduce hydrophilic/hydrophobic interactions.

The point where the surfactant starts to aggregate to form micelles is called the critical micelle concentration, CMC. From this point forward, the surface tension remains constant. The CMC value is determined from the break point in the curve where after the surface tension value remains constant. In this study the CMC was found to be 0.5 mM. This value is somewhat lower than that reported in other studies, Vincent *et al.* 2003, recorded a value of 0.8 mM, whereas, a different value of 3.1 mM was reported by Mukrjee *et al.* 1971. However, there are two fundamental differences between the referenced studies and this study. In the referenced studies SLES-2EO was used, whereas this study uses SLES with an average of 1 mole of ethoxylation as determined in the product specification. In addition, the referenced study used purified material (no characterisation information provided).

It is well reported and to be expected from theory that increasing the level of ethoxylation level will reduce the CMC. As such we should anticipate that the CMC of the material in this study should be higher than that of the previously reported study. However, the commercial SLES.1EO is a mixture of many different components. Firstly, this material contains residual electrolytes such as Sodium chloride and Sodium sulphate. Secondly, the feed stock fatty alcohol used to make the surfactant consist of approximately 75% C12 (lauryl) chains but also consist of upto 25% higher fatty alcohol chain (mainly C14 myristyl). Thirdly, the material consists of a range of ethoxylation, including higher ethoxylated materials. All of these factors would influence the CMC, driving the CMC to a lower value.

4.2.1.2 Polymer/Surfactant Mixtures

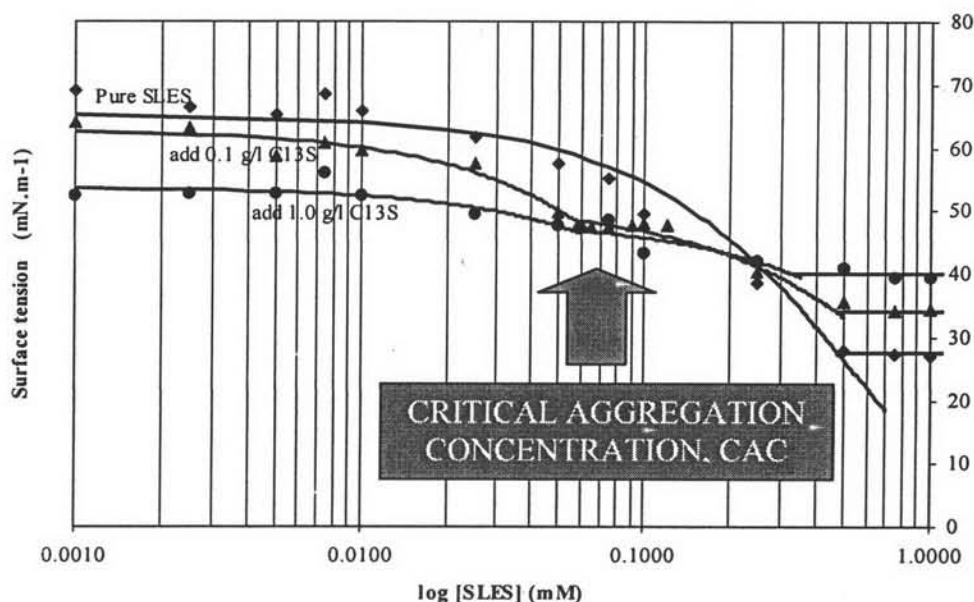


Figure 4.2 Surface tension measurements of SLES/cationic guar mixtures as a function of SLES concentration, at 30 ± 1 °C. (a) blue diamond, (b) brown triangle and (c) red circle represent SLES , SLES+0.1g/l Jaguar C13S and SLES+1.0g/l Jaguar C13S respectively. All measurements are in the absence of salt.

Figure 4.2 shows that at low surfactant concentration, the surface tension was reduced when Jaguar C13S was added. The reduction in surface tension was greater with increased polymer concentration. This result is in agreement with previous studies (Goddard *et al* 1976, Vincent *et al.* 2003). Furthermore, this observation is not surprising given that even at these low surfactant concentrations, SLES and cationic guar interact to form a complex of even higher surface activity.

At higher surfactant concentrations, the behaviour becomes more complex but does demonstrate the same trend as an ideal schematic proposed by Goddard, E.D., Ananthapadmanabhan, K.P (1993). Two break points were observed with increasing surfactant concentration. The first break point can be called the critical aggregation concentration, CAC. At the CAC the polymer-surfactant starts to interact. Additional surfactant is adsorbed by polymer in solution and hence is not effectively available for reducing the surface tension. However, the polymer-surfactant complex is slightly surface active and will have a small impact on

reducing surface tension. The CAC occurs at surfactant concentrations below the CMC. This finding was also observed by Komesvarakul, N., Scamehon, J.F. (2003).

A second break point occurs when additional surfactant is added. Whilst this nature of this break point is not clear. It could possibly represent a conformational change of the polymer-surfactant complex. This conformation change could be induced by the increased hydrophobicity of polymer-surfactant complex and may be represented by the formation of micelles on the cationic charges on the polymer. As such the conformational change may cause the polymer complex to wrap around on itself thereby eliminating the ability of the complex to reduce the surface tension. The effect appears more pronounced from higher Jaguar C13S concentrations (1g/l as compare to the lower 0.1 g/l). It was interesting that at a surfactant concentration above the CMC of the pure surfactant, the system containing Jaguar C13S showed higher surface tension values and the effect increased with Jaguar C13S concentration.

These effects might be explained by using an ideal schematic offered by Goddard, E.D., Ananthapadmanabhan, K.P (1993) where a polymer-surfactant complex could show higher surface tension at some surfactant concentration in the precipitation zone. The schematic highlights that at high surfactant concentration in a polymer-surfactant system, the surface tension is the same as that of the pure surfactant system above the CMC. Further explanation was also given by Guerrini, M.M *et al* (1998) that the coincidence with the curve is due to the complex resolubilisation at higher surfactant concentration where micelle formation occurs. In this study, the surfactant concentration was not increased sufficiently high to observe this phenomenon.

4.2.2 Phase Diagram of Cationic Guar/SLES

Solutions of Jaguar and surfactant are mixed together in a test tube to achieve the desired concentrations. The tubes are tumbled for 50 times then left to stand for two days and the evidence for flocculation/phase separation should be obtained visually. The minimum concentration of surfactant necessary to observe the phase changed from a clear, single phase to a turbid two phase region is called the critical flocculation concentration (CFC) and the (higher) concentration of surfactant

required to obtain a one-phase region again is called the critical re-solubilisation concentration (CRC).

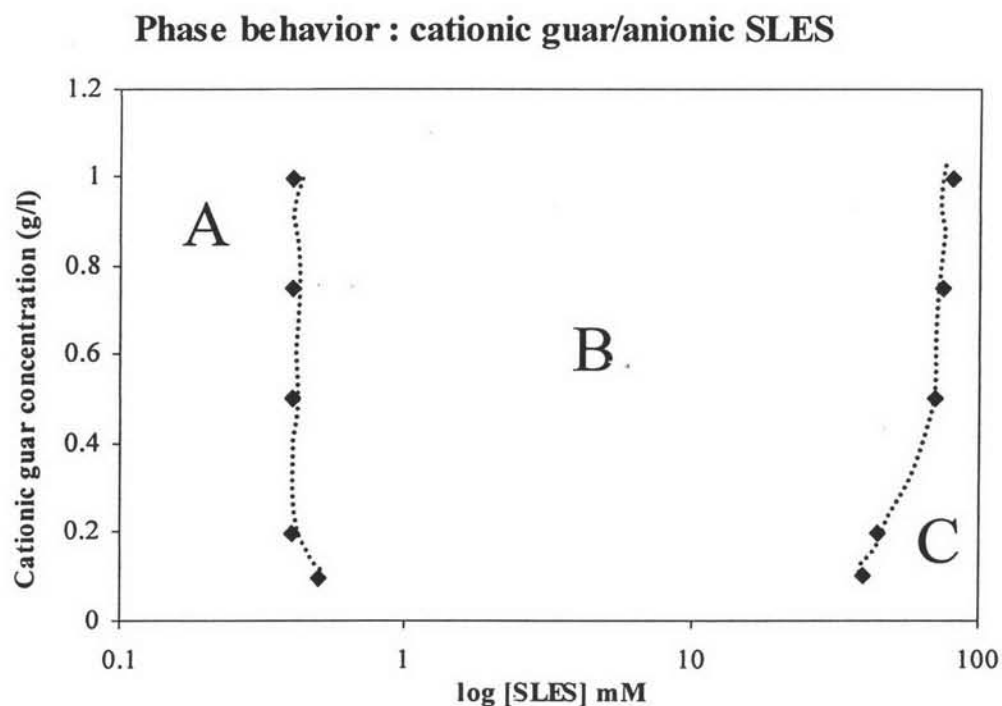


Figure 4.3 Phase diagram for solution of cationic polymer, Jaguar C13S, and anionic surfactant, SLES. The CFC and CRC are blue and red diamonds respectively at a fix sodium chloride concentration, 20 mM at 25 °C.

Figure. 4.3 shows the phase diagram of Jaguar C13S and SLES as a function of varying concentration. The critical resolubilisation concentration (CRC) and critical flocculation concentration (CFC) are illustrated in Table 4.1.

Table 4.1 Value of the CFC and CRC for different systems of cationic polymer, Jaguar C13S, and anionic surfactant, SLES

Result	Polymer concentration									
	0.1 g/l		0.2 g/l		0.5 g/l		0.75 g/l		1.0 g/l	
	CFC	CRC	CFC	CRC	CFC	CRC	CFC	CRC	CFC	CRC
[SLES] mM	0.5	40	0.4	45	0.4	70	0.4	75	0.4	80

In this work, a fixed concentration of 20 mM sodium chloride was used. This figure is typical of most commercial shampoo products. The level of sodium chloride was held constant in all samples. Moreover, it was found that Jaguar was only slightly soluble in water. At levels over 2 g/l residual, undissolved Jaguar remained in the vessel. As a result, concentrations below 2 g/l were used throughout this study. Therefore, the phase diagram was defined within a range of polymer concentrations from 0.1g/l to 1 g/l.

During this study three distinct phases were identified. Firstly, a single phase region at a low surfactant concentration (region A). Secondly, above a given surfactant concentration the solution become turbid, indicating phase separation (region B). Thirdly, an additional single phase region at high surfactant concentration was observed again (region C). This finding was in agreement with results reported by other workers (Goddard *et al.* 1976) and previous studies (Vincent *et al* 2003) have offered an explanation of these observations.

Low surfactant concentration (region A)

In this part of the phase diagram it has been proposed that the system has excess cationic polymer. As such, whilst there is association between the cationic polymer and the anionic surfactant, the cationic polymer is in excess. As a consequence the aggregate will have net positive charge rendering the polymer/surfactant complex hydrophilic and hence water soluble.

Critical flocculation concentration (refer to CFC in diagram)

As the surfactant concentration increases, the number of surfactant molecules per positive charge increases, leading to a decrease of charge on the polymer-surfactant aggregates. At some critical point (refer to as the critical flocculation concentration, CFC) the average charge on the aggregates became insufficient to solubilise the aggregates, rendering the aggregate hydrophobic. The aggregates start to combine to form supra-aggregates or flocs.

Interestingly, the CFC is quite independent of polymer concentration. Whilst this observation is counter-intuitive, it is consistent with the findings of Vincent *et al.* 2003 where they described that flocculation and hence phase

separation are not directly related to the stoichiometric charge neutralisation of the cationic polyelectrolyte by the anionic surfactants. Logically, if the flocculation boundary is solely dependent on the ratio between the surfactant and polymer then the phase boundary should increase with increasing polymer concentration. Hence this observation would suggest other factors play a role in determining the CFC. A second factor that may play an important role is the kinetics of the flocculation process. Flocculation of the polymer-surfactant aggregates is essentially a crystallisation process. The rate of crystallisation is enhanced by providing sites of nucleation. Aggregation between surfactant and polymer is essentially a dynamic process and as such at any one instant there will be exist polymer-surfactant aggregates of the correct composition to induce flocculation. If these aggregates are in sufficient concentration then a floc could be formed. A floc that is formed could act as a point of nucleation for enhancing further flocculation. Hence flocculation would occur at surfactant concentrations below the stoichiometric concentration required for a given polymer concentration.

Phase separation region (region B)

In this part of the phase diagram, turbidity and phase separation was observed. Such phase separation is entirely consistent with the model proposed by Vincent, whereby charge neutralised interaction between anionic surfactant and cationic polyelectrolyte polymer leads to the formation of hydrophobic aggregates.

Critical re-solubilisation concentration (refer to CRC in diagram)

As the surfactant concentration increases further more surfactant is absorbed into the polymer-surfactant aggregates. Consequently, the charge becomes increasingly negative. When the charge is sufficiently negative, the aggregate will become relatively hydrophilic. In addition, increased repulsion between aggregated also leads to resolubilisation of the aggregates. The concentration at which this occurs is referred to as Critical Re-solubilisation Concentration (CRC).

The results highlight that the CRC is dependent on polymer concentration. However, the dependency is not linear, for example, a ten-fold increase in polymer concentration only leads to a double of the CRC. This result is consistent with those

reported by others. (Vincent *et al.* 2003, Yamakuchi *et al.* 1999), perhaps again suggesting that kinetics has a role to play.

High surfactant concentration (region C in diagram)

At surfactant concentration higher than the CRC, the single phase region formed.

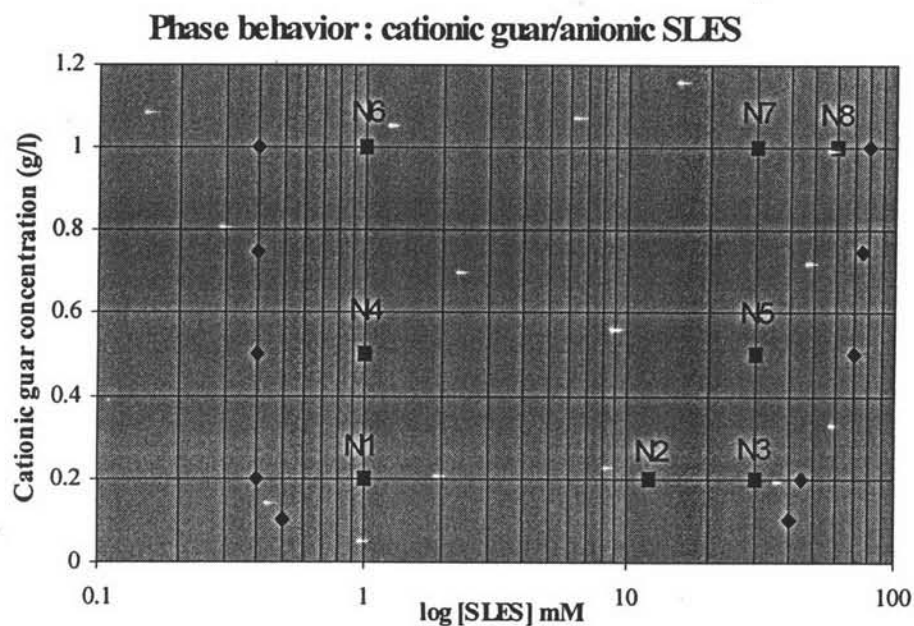


Figure 4.4 Phase diagram of the Jaguar C13/SLES system obtained during this study. Highlighting the 8 points to be used for further study.

Table 4.2 Composition of liquor used to make the flocs for future studies

Code	SLES mM	Polymer g/l	NaCl mM
N1	1	0.2	20
N2	12	0.2	20
N3	30	0.2	20
N4	1	0.5	20
N5	30	0.5	20
N6	1	1.0	20
N7	30	1.0	20
N8	60	1.0	20

Figure 4.4 and Table 4.2 illustrate the details of the eight points in the phase diagram chosen for further study. The eight points were chosen based on the variety of their positions in the phase diagram. Choosing three points of low surfactant concentration, three points of high surfactant concentration and two points of medium concentration. In addition, N8, N6 and N2 are also represented a typical dilution profile. Dilution profile refers to the fact that when the consumer uses the product, the consumer rinses creating a linear dilution curve that passes through the two-phase region.

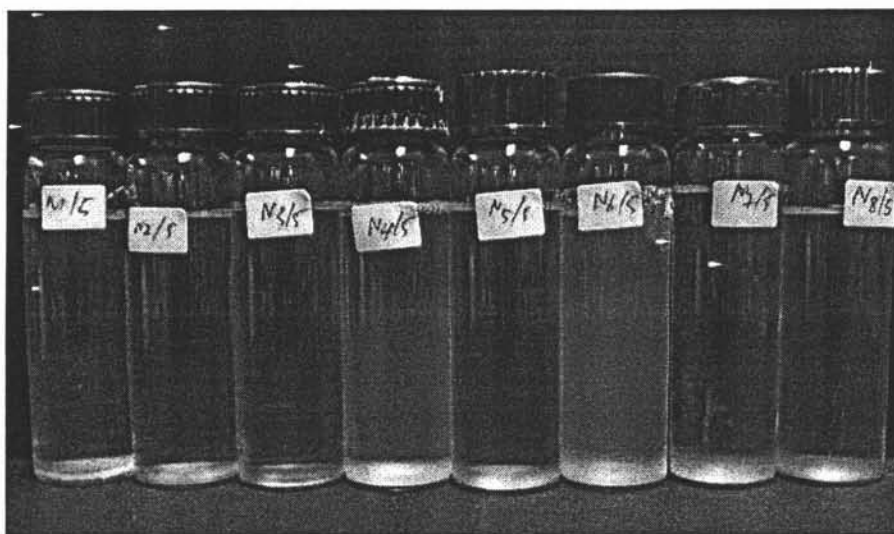


Figure 4.5 A photograph highlighting the differences in the appearance of the flocs and supernatants produced from the eight points in the phase diagram. From left to right N1 to N8. Flocs were equilibrated for 2 days.

Figure 4.5 shows photographs of the supernatants formed by preparing the eight compositions highlighted in Figure 4.4 and Table 4.2. The photographs clearly indicate some fundamental visual differences between the flocs that are produced by the eight compositions. All eight compositions produce a precipitate that sediments overtime. However, compositions N4 and N6 produce turbid solutions that fail to sediment within observed time. These compositions will now be characterised in greater depth.

4.3 Characterisation of the Aqueous dispersion of Cationic guar/SLES Aggregates

4.3.1 Floc Size Determination

Typical size distribution profiles of the eight locations on the phase diagram are illustrated below in Figure 4.6. At first glance the results indicate very little difference between the particle size profiles of the eight different locations on the phase diagram. This is most apparent when we examine the location and size of the major peak in the profile, the median size seems to only vary between 40 & 54 micron across the entire two-phase region.

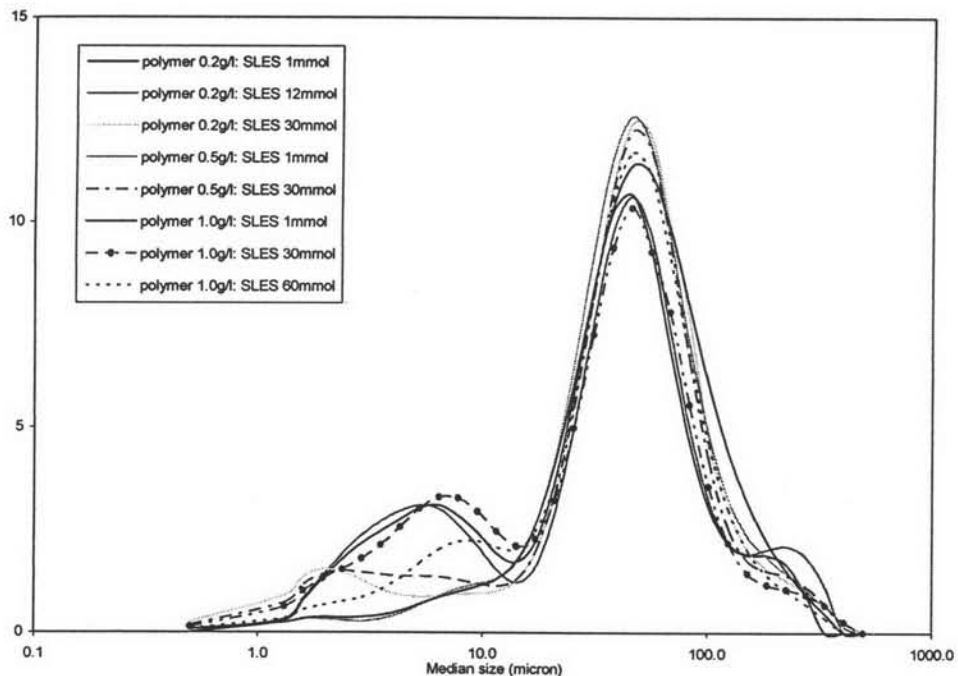


Figure 4.6 Particle size distribution profiles for flocs produced at different points in the phase diagram.

However, there are some noticeable differences in particle size distribution at the smaller particle size. The origin of these differences are not clear. Though it does seem to be apparent that this peak is at a maximum at the mid point of the two-phase region at each polymer concentration, i.e. where flocculation appears to be fastest and the flocs formed are most hydrophobic. For example, this peak is

maximum at 1 & 12mmol SLES for a polymer concentration of 0.2g/l and 30mmol SLES for 1g/l polymer concentration. Interestingly, this smaller peak is at a minimum when the flocs tend to be cationic, see below.

In addition, if we examine the floc size at a constant floc age as a function of composition we can identify some clear trends. Median size as measured at a floc age of 10mins as a function of polymer and SLES concentration is illustrated in Figures 4.7 and 4.8 respectively.

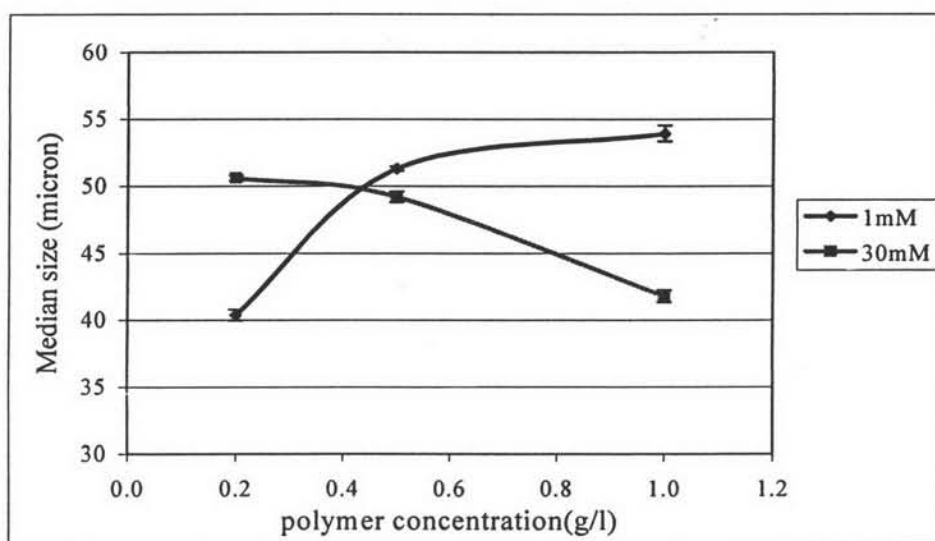


Figure 4.7 Floc median particle size as a function of polymer concentration for two different surfactant concentrations (1mM & 30mM) as measured at a constant floc age (10mins).

Figure 4.7 illustrates a clear dependency on floc size as a function of polymer concentration. However, the trend appears to be different for different surfactant concentrations.

At low surfactant concentrations the floc size increases with increasing polymer concentration. This observation would suggest floc formation and growth in this region of the phase diagram where polymer is in excess occurs firstly through the precipitation of floc that has a higher SLES/polymer ratio than that existing in the

bulk. Floc growth then occurs through the addition of the excess polymer perhaps precipitated with a low ratio of SLES.

At higher surfactant concentrations the floc size decreases with increasing polymer concentration. This observation for the region of the phase diagram where surfactant is in excess compared to polymer is consistent with the explanation given for the low surfactant concentration. The results would suggest that floc formation firstly occurs by precipitation of floc which contains an SLES/polymer ratio again which is lower than exists in the bulk. Floc growth then occurs through the precipitation of excess SLES, or floc with a high SLES/polymer ratio.

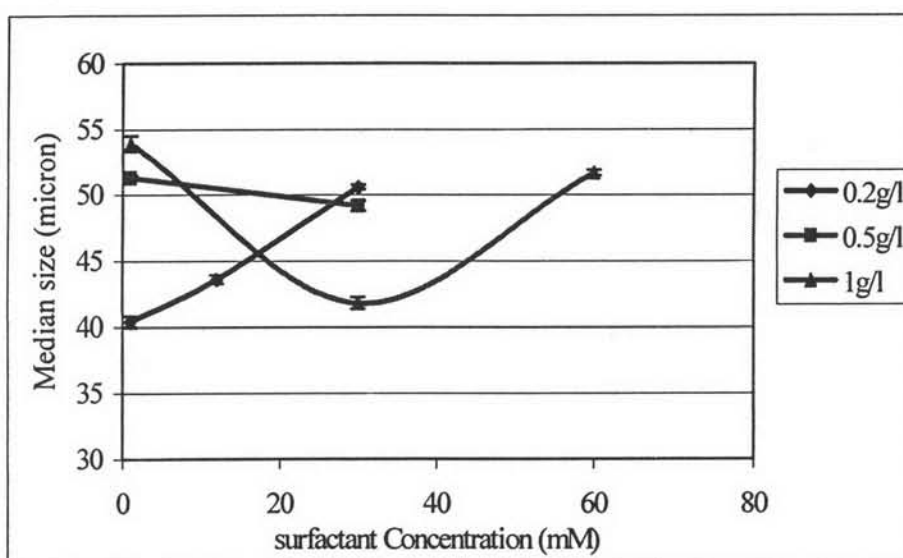


Figure 4.8 Floc median particle size as a function of surfactant concentration for three different polymer concentrations (0.2, 0.5 & 1.0g/l) as measured at a constant floc age (10mins).

A graph showing the relationship between floc median size as a function of surfactant concentration at different polymer concentrations at a constant floc age is shown in Figure 4.8. The graph clearly indicates that the relationship between floc size and surfactant and polymer concentration is complex.

At low polymer concentration the floc size increases with increasing surfactant concentration. This is consistent with the hypothesis proposed above. In that floc size is at a minimum when neither the polymer nor surfactant is in excess but rather there is a stoichiometric amount of polymer and surfactant. The particle size will increase with increasing surfactant concentration as floc growth will occur with precipitated floc that is rich in surfactant compared to polymer.

At intermediate polymer concentration the floc size appears to be largely independent of surfactant concentration.

At higher polymer concentration a clear minimum in particle size is observed for increasing surfactant concentration. This result is again in agreement with the proposed hypothesis. At high polymer concentration, low surfactant concentration the polymer is in excess in floc growth occurs through precipitation of polymer/surfactant complex which is rich in polymer onto floc that has the stoichiometric ratio of polymer and surfactant. Floc size is at a minimum when the concentrations of surfactant and polymer in the bulk is close to the stoichiometric ratio of polymer and surfactant. The floc size then again increases with increasing surfactant concentration as polymer/surfactant complex which is rich in surfactant deposits onto the stoichiometric floc.

This observation is consistent with the idea that floc formation initially occurs through the precipitation of surfactant/polymer complex at a stoichiometric ratio, i.e. when the complex is most hydrophobic. When the complex is most hydrophobic it is more energetically favourable for precipitation to occur, hence precipitation will occur rapidly and at many more locations throughout the sample. As a consequence, the floc size will be smaller as precipitation will be too rapid to allow growth on the initial precipitated flocs.

However, where the polymer/surfactant ratio is very high or very low it is anticipated that floc growth will be more rapid. At time=0 when the polymer and surfactant is first mixed it is anticipated that the first flocs to form and precipitate will have a composition close to the stoichiometric optimum ratio of polymer/surfactant ratio as precipitation of a complex at this ratio would be most energetically favourable. The remaining polymer/surfactant complex will be relatively hydrophilic due to the non-stoichiometric composition in the bulk. As a

consequence it will be less energetically favourable for this complex to precipitate, so precipitation will be slower and will only occur through growth on the flocs already precipitated, which would act as sites of nucleation for the floc growth process. Hence it is anticipated that non-stoichiometric mixes in the bulk will produce flocs with a larger particle size.

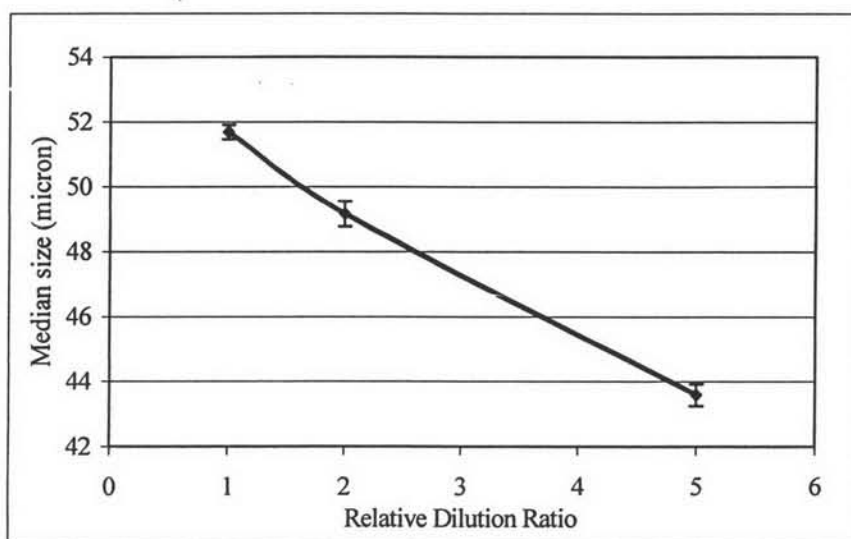


Figure 4.9 Floc median size at a constant polymer/surfactant ratio, expressed as relative dilution as measured at a constant floc age (10mins).. 1g/l & 60mM is taken as a dilution of 1.

Figure 4.9 examines floc size at a constant polymer/surfactant ratio as a function of relative dilution. It is apparent that there is a strong relationship between floc size and total concentration of polymer & surfactant, for a non-stoichiometric mix of polymer and surfactant. The particle size decreases rapidly with decreasing concentration. This is to be anticipated as the rate of floc growth would be dependent on the rate of precipitation of polymer/surfactant complex on the sites of nucleation. The rate of precipitation will in turn depend upon the concentration in the bulk. This finding is in agreement with the work done by Jian-jun Zhang *et al* (2003), who demonstrated a higher initial concentration produced more, large

aggregates with a higher peak concentration. Additionally, the peak size increased almost linearly when dynamic steady state was achieved.

4.3.2 Determination of Floc Electrophoretic Mobility

The results indicate a clear trend across the two-phase region. The electrophoresis mobility appears to be highly dependent upon the SLES/Cationic polymer ratio used to form the flocs. Figures 4.10 and 4.11 illustrate the results of the electrophoresis mobility as a function of either the polymer concentration or the surfactant concentration.

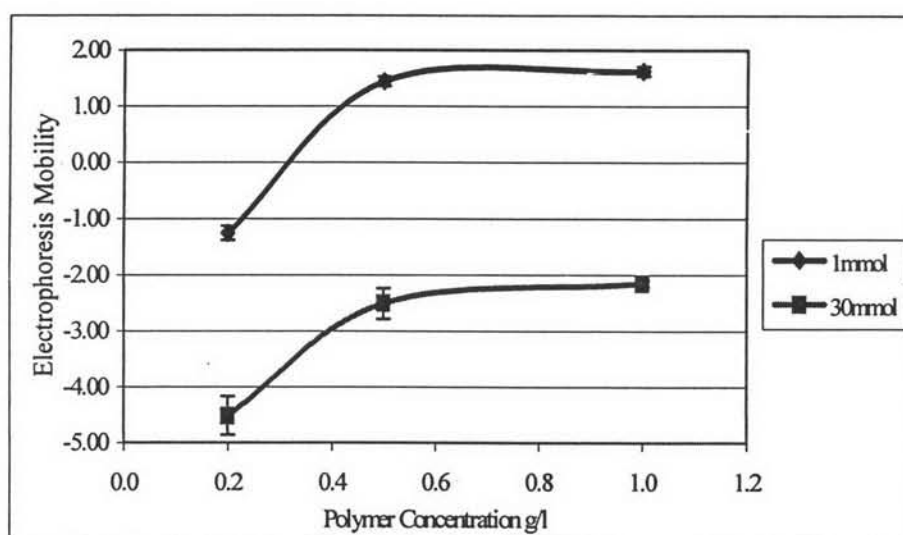


Figure 4.10 Electrophoresis mobility as a function of polymer concentration for two different levels of surfactant solution.

Figure 4.10 illustrates that as the polymer concentration increases there is an initial increase in the electrophoresis mobility. It is assumed that this is a direct consequence of increasing polymer adsorption into the isolated flocs, thereby contributing to increasing the charge (i.e. less negative or more positive) of the floc. This observation is in agreement with both dry weight extract of floc and the chemical composition of the isolated floc (S/N). However, the results also indicate that at polymer concentrations of greater than 0.5g/l there is little further increase in the electrophoretic mobility regardless of the polymer concentration. This result is

again in agreement with the chemical composition of isolated flocs, as the S/N ratio does not change with increasing polymer concentration above a polymer concentration of 0.5g/l.

In addition, Figure 4.10 shows clear differences between the two surfactant concentrations of 1mmol and 30mmol. The 1mmol surfactant concentration has an increased value (i.e. reduced negative value or increased positive value) compared to the 30mmol surfactant concentration for all polymer concentrations. This result is to be anticipated and would suggest a difference in the amount of SLES that is bound into the flocs. This observation is confirmed below, where the S/N ratio is consistently higher for the 30mmol surfactant concentration.

One further observation to be made, is that by exploring such a wide area within the two-phase region we have identified flocs with a wide-range in electrophoretic mobility. At high polymer, low surfactant concentrations we have produced flocs which are cationic in nature. Whereas, this study has also identified some points on the phase diagram which produce flocs that have a low charge density, as well as points with a high charge density.

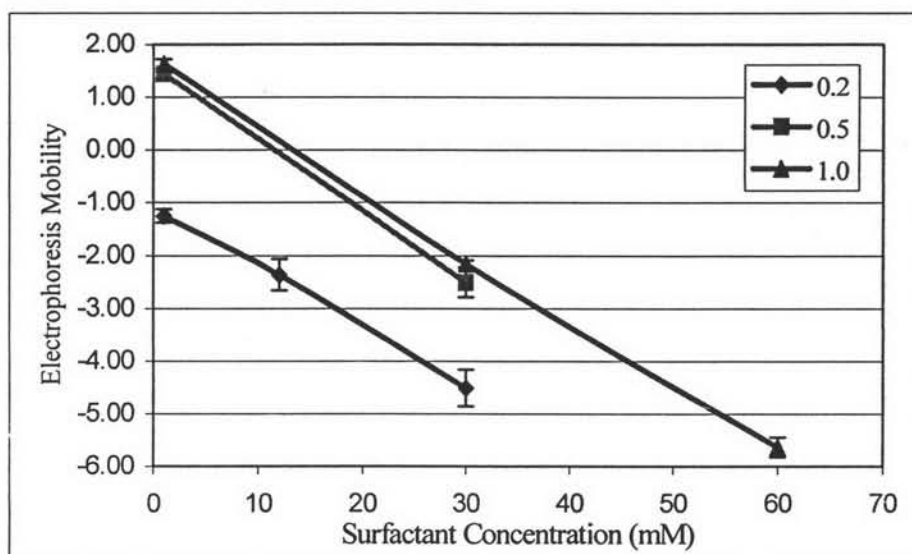


Figure 4.11 Electrophoresis mobility as a function of surfactant concentration for three different levels of polymer concentration at 0.2, 0.5 and 1 g/l.

In Figure 4.11 the relationship between electrophoretic mobility and surfactant concentration is transparent. As the surfactant concentration is increased the electrophoretic mobility becomes more negative, this is true for all polymer concentrations. In addition the gradient of the graph appears to be constant whatever the polymer concentration. This observation would tend to suggest that the degree of binding of SLES (with increasing SLES concentration) is largely independent of the polymer concentration. This observation is consistent with other results discussed in this Chapter. For example, it is shown below that the dry weight of extracted floc increases with increasing polymer concentration, however, particle size results suggest that this is not a consequence of larger floc sizes, hence it must indicate an increase in the number of floc particles. In the electrophoretic mobility experiments we are measuring the mobility of individual particles, hence the observed effect is independent of the number of particles and also the polymer concentration, but rather is just dependent on the ability of the surfactant to bind to that polymer. Providing that this binding is not saturated it will be independent of the polymer concentration.

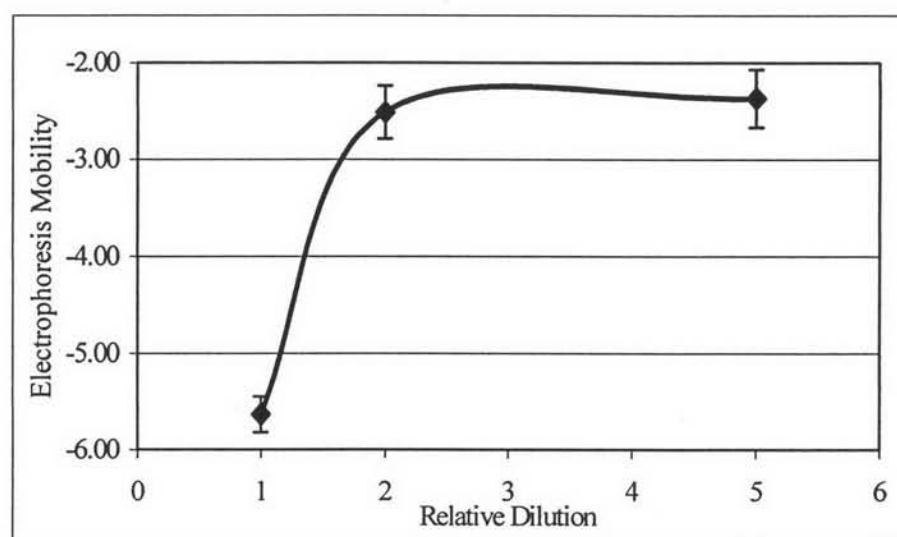


Figure 4.12 Electrophoresis mobility as a function of relative dilution. In this graph the SLES/polymer ratio is kept at 60:1, i.e. at a relative dilution of 1, the SLES concentration is 60mmol & polymer concentration is 1g/l. At a relative dilution of 2, the SLES concentration is 30mmol and polymer concentration is 0.5g/l.

Figure 4.12 indicates that under a constant SLES/polymer ratio the electrophoretic mobility will depend, to some extent, on the total concentration in the sample. At lower concentrations the electrophoretic mobility is independent of solids concentration. This result is to be anticipated given the discussion above, i.e. that in this experiment it is the mobility of an individual particle that is being measured. However, at higher concentrations, it is apparent that the mobility is higher than anticipated, perhaps suggesting some kind of co-operative binding of SLES that is dependent on the total solids concentration.

4.4 Characterisation of Isolated, Dry Cationic Guar/SLES Aggregates

4.4.1 Determination of Weight of Dry Extracted Floc

The dry weight of extracted flocs of various points in the two phase region isolated by the centrifuge method described in the experimental section is shown in Figure 4.13. The results indicate that the isolated weight of floc is at a minimum close to the phase boundary, and tends to be at a maximum in the mid region in the phase diagram. This result is perhaps not surprising and tends to reinforce the hypothesis that the phase boundary identified in this study is driven more by kinetics (crystallisation nucleation) rather than chemical equilibrium.

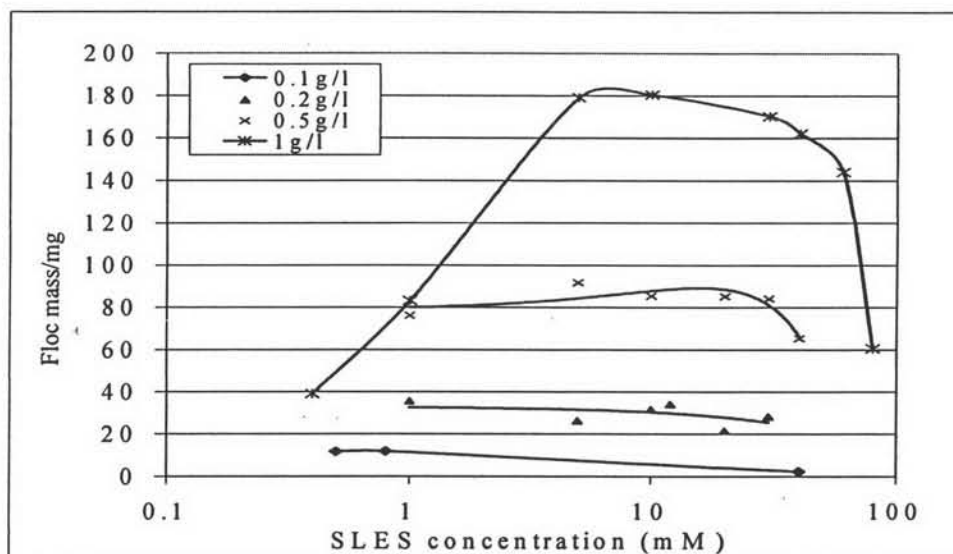


Figure 4.13 Dry weight of isolated floc from selected points in the precipitated, two phase region for different polymer concentrations as a function of surfactant concentration.

However, it is also apparent that the weight profile is different for each different polymer concentration. At low polymer concentrations the maximum weight of dried floc is attained relatively close to the phase boundary and remains constant over a high range of surfactant concentrations. This would suggest that at these low polymer concentrations within a given polymer concentration the surfactant is in large excess. In this instance the fact that the dried floc weight is independent of surfactant concentration would suggest that the surfactant molecules are absorbed into the flocs at some optimised ratio, i.e. an optimised number of surfactant molecules per polymer cationic charge.

At higher polymer concentrations, it is apparent that the maximum weight of dried, isolated floc occurs at a surfactant concentration significantly higher than at the phase boundary. This observation would suggest that at these higher polymer, lower surfactant concentrations the polymer is in excess and hence the weight of isolated floc will be dependent on the surfactant concentration. The weight of isolated floc will tend to increase with increasing surfactant concentration until some

optimised surfactant per polymer cationic charge is attained. At this point, the weight of isolated floc would remain constant.

This analysis would suggest that for a given surfactant concentration, the weight of isolated, dried floc would be highly dependent on the polymer concentration. Extracted, dried floc weight as a function of polymer concentration for a constant surfactant concentration is illustrated in Figure 4.14. The results do indeed indicate that the extracted, dried floc weight is highly dependent on the polymer concentration. This result is in agreement with a previous report by Vincent *et al* 2003.

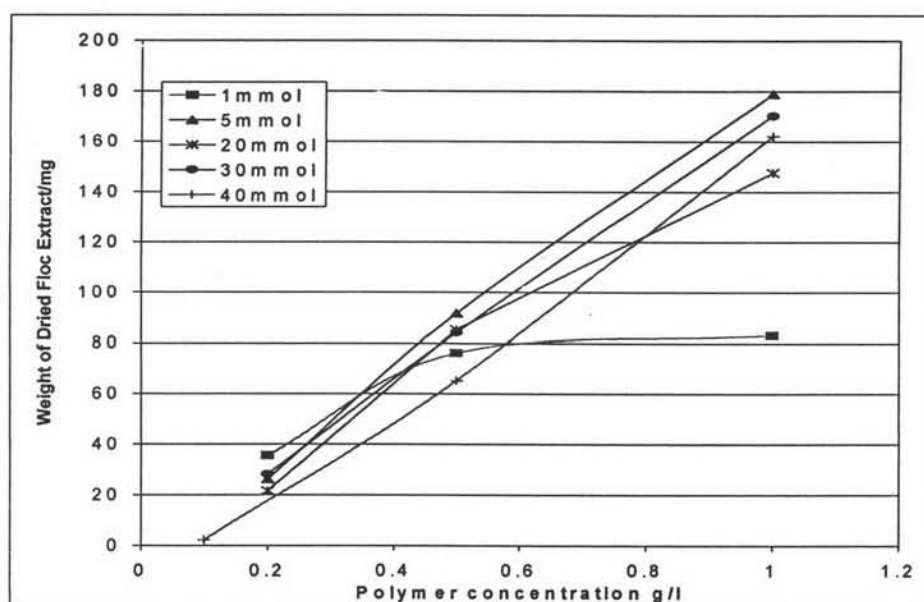


Figure 4.14 Weight of dried floc extract as a function of polymer concentration for a given surfactant concentration.

Figure 4.14 also indicates that for low surfactant concentrations (1 mmol) the weight of dried floc extract becomes independent of polymer concentration, at higher polymer concentrations. Indeed indicating that the polymer is in excess.

4.4.2 Chemical Composition Determination by FTIR

In order to confirm that the isolated flocs consist of anionic SLES and cationic polymer Jaguar C13S, FTIR spectra of isolated flocs were conducted. The spectra are illustrated below in Figure 4.15

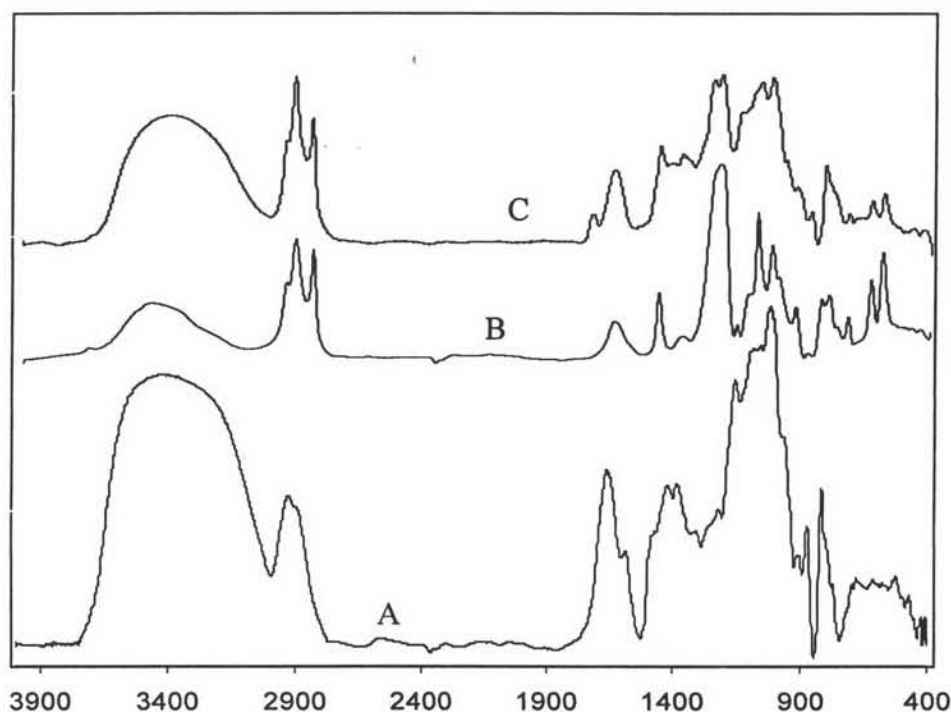


Figure 4.15 FTIR spectra of (A) pure cationic guar polymer Jaguar C13S, (B) pure anionic surfactant, SLES and (C) extracted dry flocs contained SLES (30 mM), Jaguar C13S (0.2 g/l) and NaCl (20 mM).

In the spectra of polymer Jaguar C13S (A in Figure 4.10) the stretch of the O-H bond on the carbohydrate rings at approximately 3400 cm^{-1} is clearly visible. Moreover, a very intense characteristic peak appears at 1018 cm^{-1} which correspond to the C-O stretching in alcohol further aids confirmation of the structure of Jaguar C13S. The C-O bonds in Jaguar exist in both mannose and galactose subunits.

The spectra of anionic SLES (B) clearly identifies a strong characteristic peak of S=O stretch at approximately 1200 cm^{-1} , reminiscent of the sulphate group of the surfactant headgroup. Moreover, the spectra indicates a peak at 1080 cm^{-1} , that corresponds to a C-O stretch in ether linkages indicated the presence of ethoxylated

group in the material. The spectra of the isolated flocs (C) demonstrate characteristics of both SLES and Jaguar, as can be illustrated by the presence of both the S=O stretch (1200 cm^{-1}) of SLES and the O-H stretch (3400 cm^{-1}) of Jaguar. The results indicate that the flocs contain both polymer and surfactant as the flocs showed the combination of both spectra from both pure polymer and pure surfactant.

4.4.3 Determination of Chemical Composition: Sulphur/Nitrogen Ratio

The vacuum dried flocs were used for elemental analysis to determine the sulphur (one atom in each surfactant molecule) and nitrogen (one atom for each cationic centre on the polymer) levels. The ratio between the molar percentage of sulphur and nitrogen can be then calculated to obtain the average number of surfactant molecules bound per cationic centre in the floc. However, such a calculation is based on the assumption that all the nitrogen atoms in Jaguar exist as quaternary cationic. The results are illustrated in Figures 4.16.

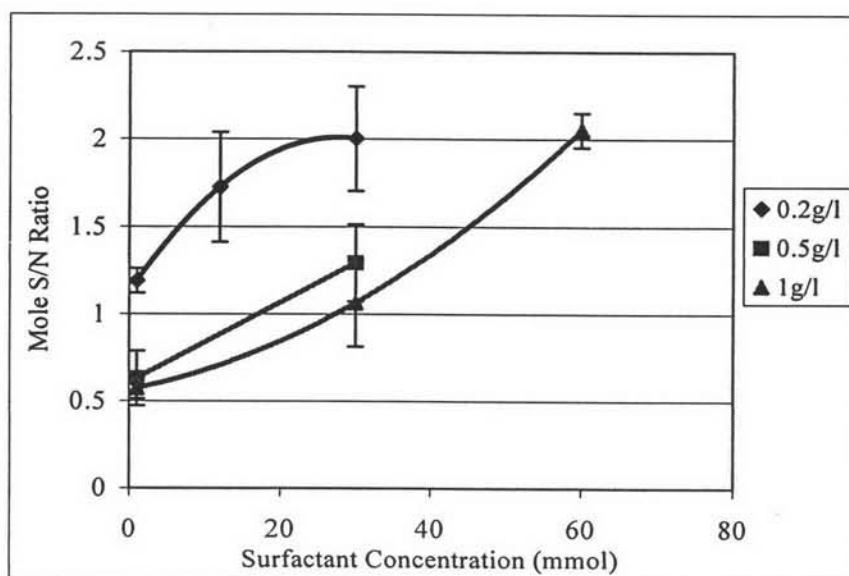


Figure 4.16 Sulphur/Nitrogen ratio of dried, isolated flocs as a function of surfactant concentration for constant polymer concentrations.

As expected, Figure 4.16 highlights that on the whole the mole ratio of sulphur to nitrogen increases as a function of surfactant concentration. This is assumed to be a consequence of more anionic surfactant molecules binding per cationic site. This result is true for all polymer levels.

However, the Sulphur/Nitrogen results are inconsistent with the hypothesis suggested in section 4.4.1. In Section 4.4.1 it was suggested that the S/N ratio should be constant across the two phase region (constant polymer concentration) within the region where the weight level of precipitated floc is constant. The results in this section suggest that within the constant floc weight region the S/N ratio increases (consistent with the work of others). As such this would suggest that increasing the surfactant concentration results in reducing the precipitation of the cationic polymer, probably a consequence of increasing the amount of surfactant/polymer complex which has sufficient charge in order to induce resolubilisation of the complex.

In addition, it can be identified that the S/N ratio decreases with increasing polymer concentration for all surfactant concentrations. This is illustrated in Figure 4.17. This result is to be anticipated, as the higher polymer concentration will inevitably lead to higher incorporation of polymer into the flocs. In Figure 4.17 it is also apparent that there is a minimum surfactant/polymer ratio which can induce flocculation. However, this minimum appears to be dependent on the surfactant concentration in the bulk. At the low surfactant concentration of 1mmol, this minimum ratio occurs at 0.5, whereas at 30mmol it occurs at 1, hence suggesting that there is no universal ratio of surfactant/polymer ratio which will induce flocculation but rather that the ratio is context specific.

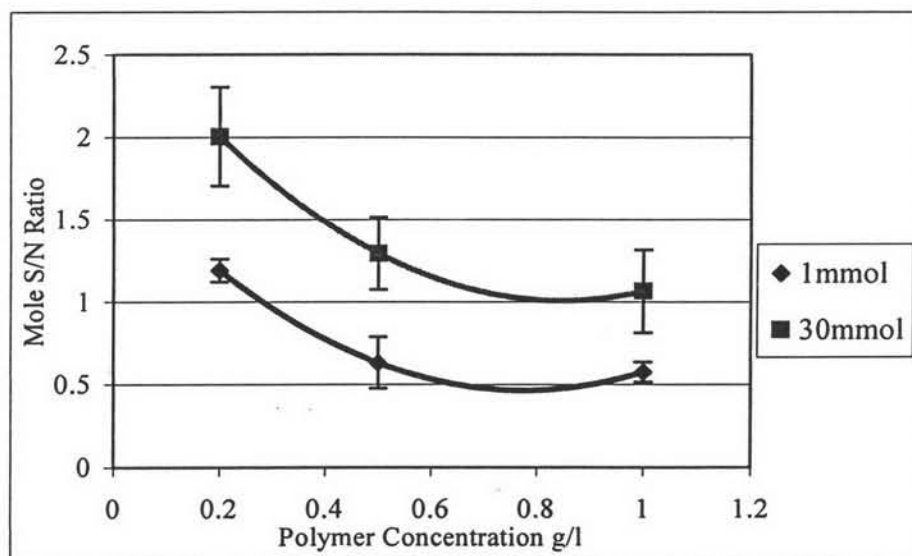


Figure 4.17 Sulphur/Nitrogen ratio of dried, isolated flocs as a function of polymer concentration for constant surfactant concentration.

4.4.4 Determination of Floc Topography: Scanning Electron Microscopy

4.4.4.1 *Effect of Drying Method*

Two different drying methods were used in order to investigate the difference in morphology of the isolated flocs :

- 1) Oven drying under vacuum at 40°C
- 2) Freeze-drying method

Flocs sample for this study were prepared at the concentration of SLES 30 mM, 0.2 g/l Jaguar and 20 mM NaCl. Figure 4.18 and Figure 4.19 showed the results of these two processes respectively. The pictures indicate that the structure of the flocs depend on the condition used to dry them. Freeze-drying provides a sudden freezing to the solution, reducing molecular motion such that the original structure is frozen in ice. The ice is then removed through sublimation under vacuum, hence maintaining the original structure. The morphology obtained highlights the formation of a network (presumably made from the polymer/surfactant complex) and voids.

Freeze drying is clearly the best method to identify the difference in the morphology of flocs as they exist in the aqueous suspension. SEM photographs of freeze-dried flocs prepared by different processes are shown below.

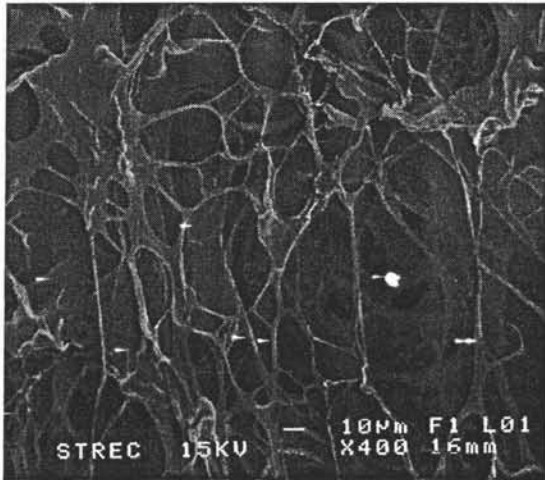


Figure 4.18 A Typical structure of flocs after freeze-drying .

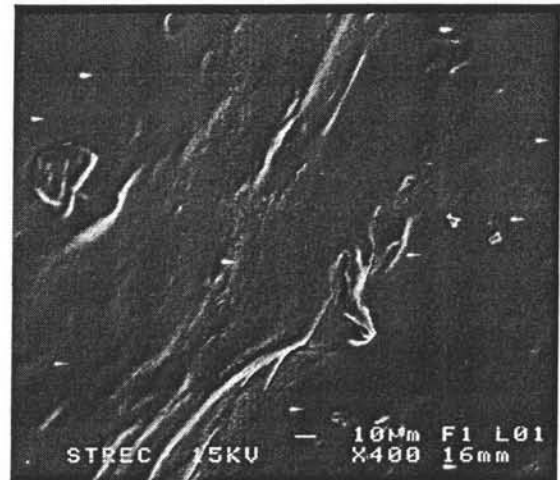


Figure 4.19 The structure of flocs after oven drying under vacuum at 40°C.

The SEM photograph of flocs dried under vacuum condition is shown in Figure 4.19. The micrograph clearly indicates a structure or morphology that is very different from that obtained by freeze-drying. In addition, this morphology tends to be independent of processing conditions, i.e. how the flocs are prepared and also the composition in the two-phase region used to make the flocs. The micrograph clearly indicates a collapsed, smooth film structure.

The vacuum drying process was used for all future studies as this drying method is much more consistent with the consumer hair drying experience.

4.4.4.2 Effect of Agitation Speed

SEM photographs of freeze-dried flocs prepared by different processes are shown below in Figure 4.20. Figure 4.20 shows that different floc morphologies occur when the flocs are prepared by using different stirrer speeds (flocs composed of SLES 30 mM, 0.2 g/l Jaguar C13S and 20 mM NaCl). The results suggest that using high agitation speed produces a more open floc structure with thinner walls, whereas low speed agitation results in larger voids with thicker

walls. From a consumer perspective the implication is that the more vigorously the consumer rubs their hair during application then the tighter, thinner walled floc would be produced. However, it is apparent that under the more realistic consumer conditions of drying at atmospheric pressure there would be little difference in the appearance of the floc regardless of the agitation speed used.

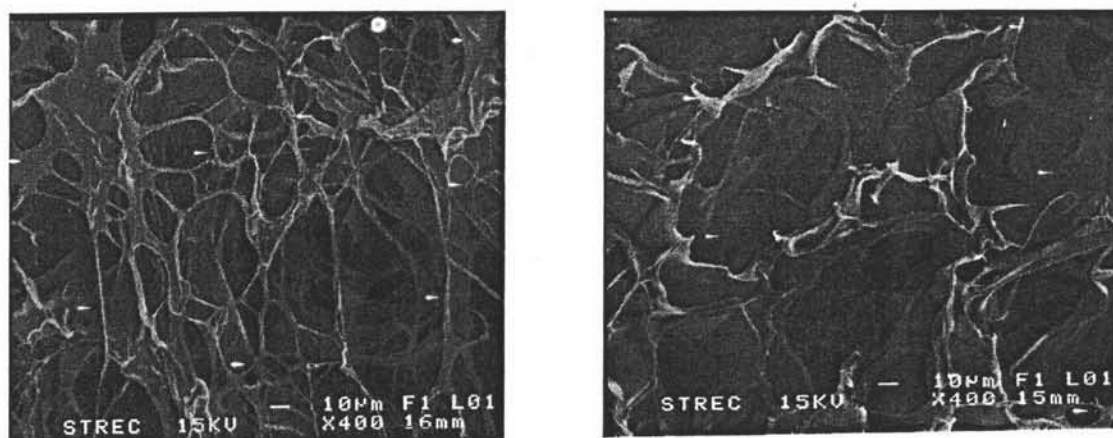


Figure 4.20 Floc morphologies identified by SEM prepared by freeze drying at different agitation speed. Flocs were prepared at a composition of SLES 30 mM, 0.2 g/l Jaguar C13S and 20 mM NaCl. Left, flocs prepared under high speed agitation: Right, flocs prepared under low speed agitation.

4.4.4.3 Effect of Polymer Content

Figure 4.21 shows different floc morphologies when the flocs are prepared at different polymer concentrations by the freeze-drying process at constant agitation speeds and constant surfactant concentration. The results suggest that the flocs have more dense structure and become more continuous with less voids when polymer concentration is increased from 0.2, 0.5 and 1.0 g/l.

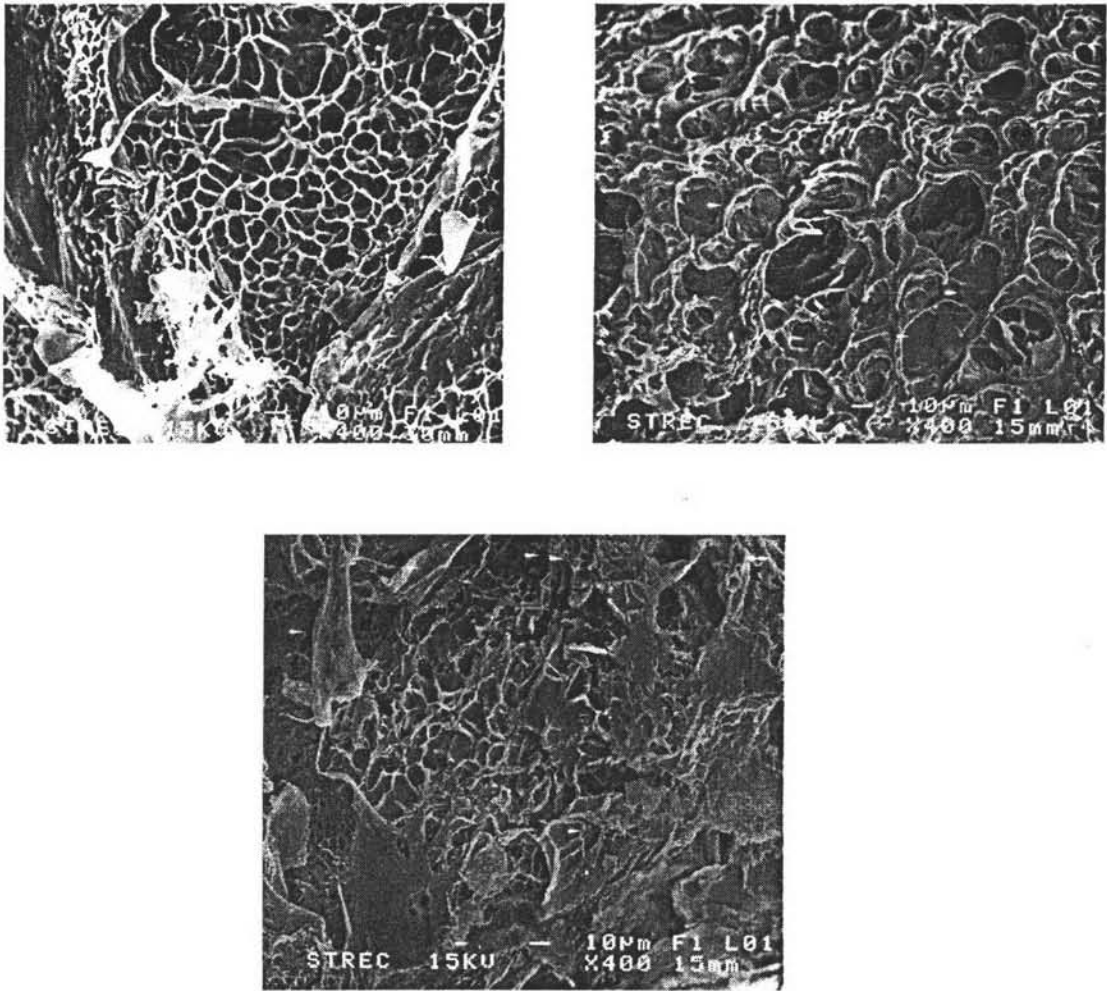


Figure 4.21 Floccs prepared by freeze drying and studied by SEM as function of polymer concentration. Floccs prepared under constant surfactant and NaCl (1mM and 20mM respectively) using the same agitation. Polymer concentration was 0.2g/l, 0.5g/l and 1.0 g/l for the samples top left, top right and bottom respectively.

4.4 Inter-relationships Between Different Characteristics

4.4.1 Floc Size and Floc Charge

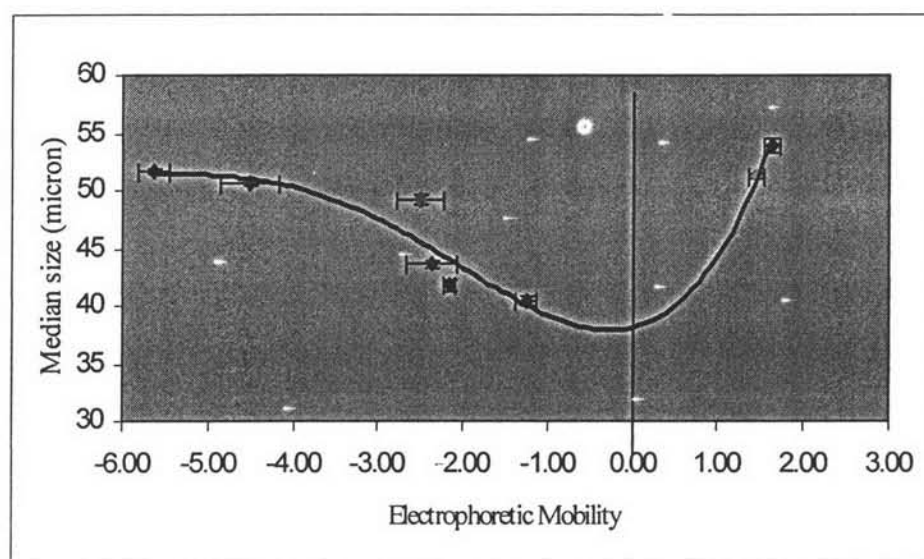


Figure 4.22 Median Particle Size as a function of electrophoretic mobility. The three different polymer concentrations are highlighted: Blue – 1g/l, green – 0.5g/l and red - 0.2g/l.

The results shown in Figure 4.22 are entirely consistent with the hypothesis suggesting that the floc size will be dependent upon the ratio of SLES/polymer. The hypothesis suggested that where there is an optimum, stoichiometric ratio between SLES and polymer, flocculation would be fastest and occur simultaneously in many more locations throughout the sample, thereby limiting the particle size. It can also be postulated that at this stoichiometric optimum the flocs would be most hydrophobic. Flocculation will be fastest at an SLES/cationic polymer ratio where it is most energetically favourable for the complex to be precipitated, i.e. where there is a maximum difference in hydrophilicity between the medium (aqueous solution) and the polymer/surfactant complex. This would occur when the polymer/surfactant complex is most hydrophobic, i.e. at the point of zero charge or zero electrophoretic mobility.

4.5.2 Floc size and Weight Dry Floc

If we consider the full sample of eight points there is no obvious inter-relationship between the floc size and the weight of dry floc extracted. However, given that it is apparent that the weight of dry floc is highly dependent on the polymer concentration it would seem appropriate to examine the relationship of floc size with weight of dry floc extract under constant polymer concentration. In addition, it would seem appropriate to consider this inter-relationship under constant polymer/surfactant ratio. These results are illustrated in Figure 4.23.

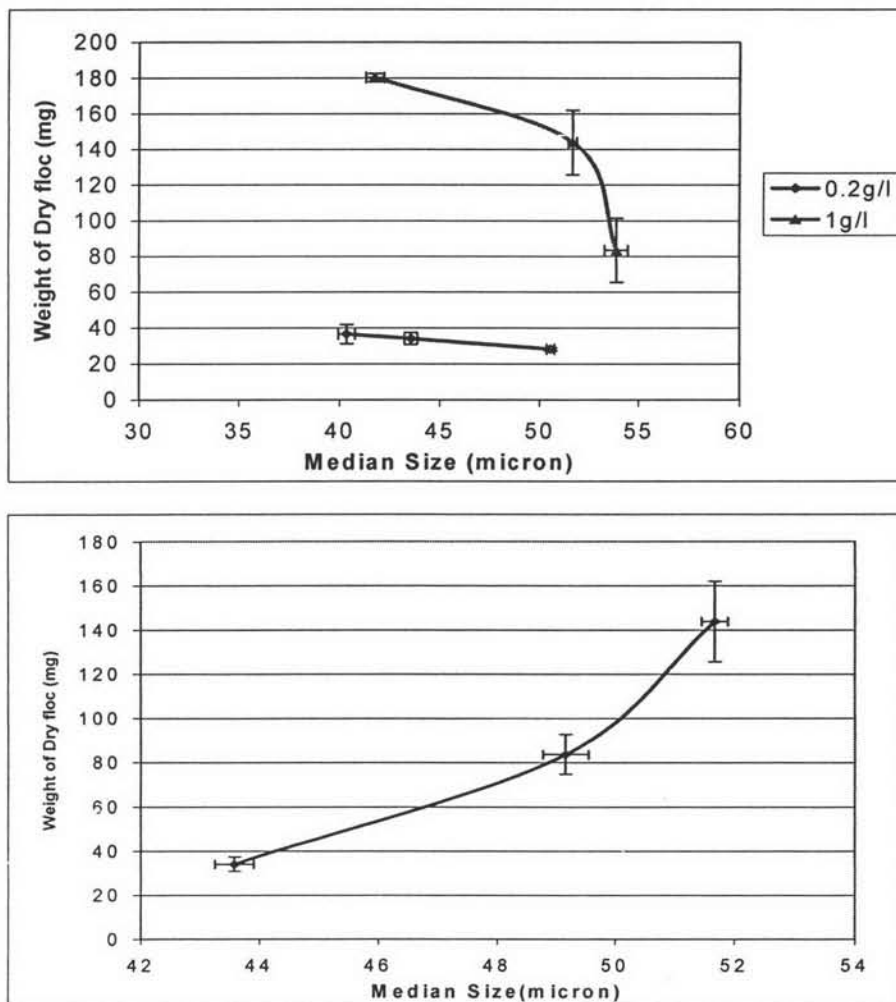


Figure 4.23 Graphs examining the inter-relationship between weight of extracted dry floc and particle size. Top – under constant polymer concentrations, bottom under constant polymer/surfactant ratio.

Figure 4.23 illustrates that under constant polymer concentration the weight of extracted floc decreases with increasing particle size. These results are to be anticipated as it was previously identified that the floc size is at a minimum when the ratio of polymer/surfactant concentration approaches a stoichiometric ratio. At this ratio, the flocs produced should be most hydrophobic and as such it is most energetically favourable for precipitation to occur.

Figure 4.23 also illustrates that at constant polymer/surfactant ratio the weight of dry extracted floc increases with increasing particle size. This inter-relationship is simply a reflection of strong relationship between weight of dry floc with polymer concentration and also the relationship of increasing particle size with increasing polymer concentration under constant polymer/surfactant ratio.

4.5.3 Floc size and Chemical Composition

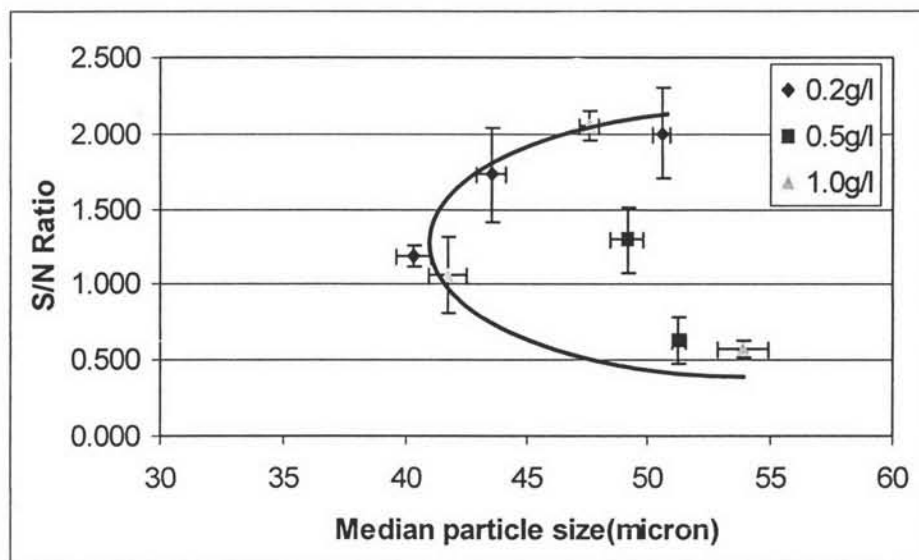


Figure 4.24 The inter-relationship between floc size and floc chemical composition

Figure 4.24 illustrates the relationship between median particle size and the chemical composition, S/N ratio. The results illustrate that with the exception of the point at a polymer concentration of 0.5g/l and SLES concentration 30mmol there is a clear trend. The particle size is largest at minimum and maximum S/N ratio, i.e.

where the flocs are most highly charged and at a minimum at a S/N ratio of approximately one, i.e. where there the floc is most hydrophobic.

This observation is in agreement with the explanation discussed previously. Floc precipitation would be expected to be most rapid when the floc is most hydrophobic, i.e. at a S/N ratio of approximately unity. In regions of rapid flocculation, floc growth is expected to be limited as precipitation of the polymer/surfactant complex will occur at many more locations throughout the sample, resulting in many more sites of nucleation/crystal growth but less material in the bulk available for crystal growth.

4.5.4 Floc Charge and Dry Weight of Isolated Floc

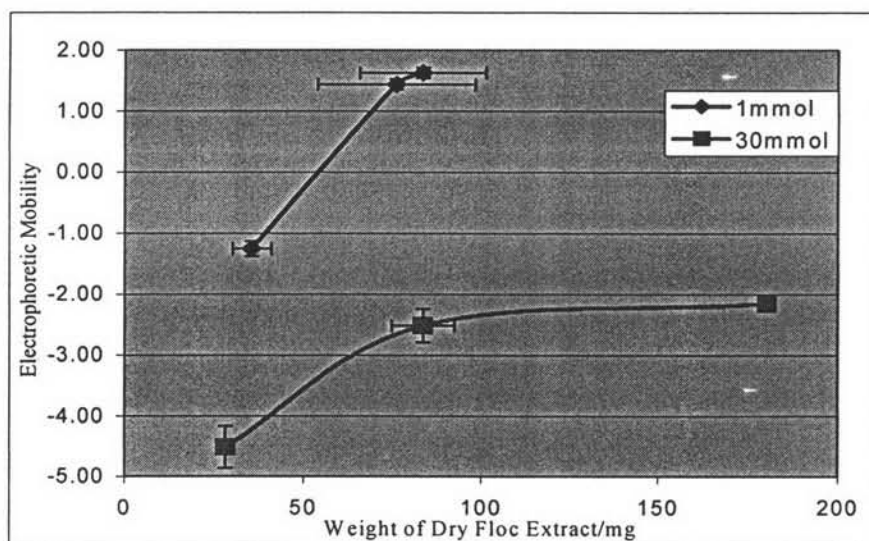


Figure 4.25 Relationship between electrophoretic mobility and weight of dry extract of floc for the two different surfactant levels.

Figure 4.25 illustrates the relationship between Electrophoretic mobility and the weight of dry extracted floc. The results indicate a trend that as the weight of dry floc extract increases then so does the electrophoretic mobility, i.e. becomes less negative or increasingly positive. The graph in Figure 4.25 is very similar to that identified previously where the relationship between electrophoretic mobility and polymer concentration was investigated. This is perhaps not surprising given the

strong relationship between polymer concentration and weight of dry extracted floc that was identified earlier.

In reality no relationship between the extracted dry weight of floc and electrophoretic mobility would be anticipated. As has been discussed previously, it is apparent from the particle size data that increasing the mass of the floc extracted does not have a particularly large impact on the size of the flocs formed, as such this would tend to indicate that the number of floc centres would increase with increasing mass of floc extracted. As the electrophoretic mobility measurement is based on measuring the mobility of individual particles it is to be anticipated that mobility would largely be independent of weight of floc.

4.5.5 Floc Charge and Chemical Composition of Floc

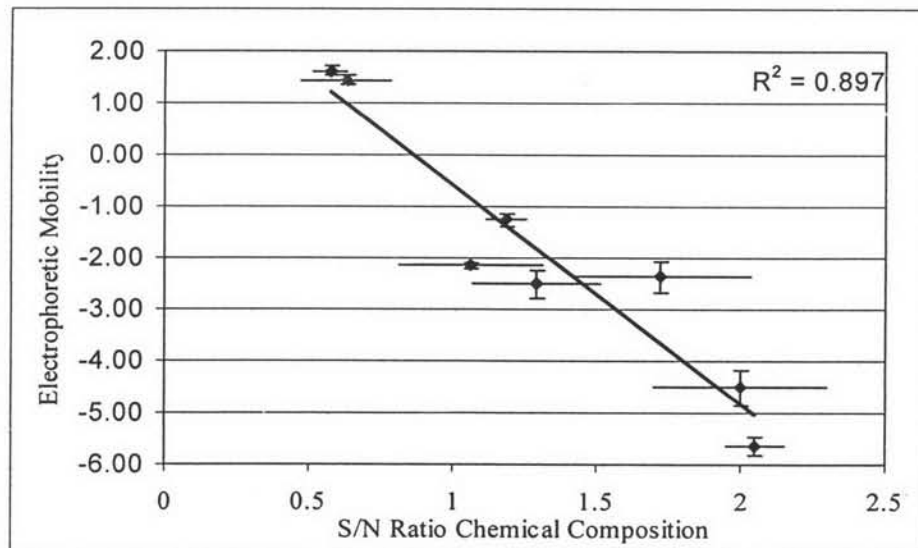


Figure 4.26 The relationship between electrophoretic mobility and chemical composition of the floc (S/N ratio). Different polymer concentrations are illustrated: blue – 1g/l, green - 0.5g/l and red – 0.2g/l.

Figure 4.26 illustrates the relationship between the chemical composition (S/N ratio) of the isolated flocs and the electrophoretic mobility. The results indicate a strong inter-relationship between the two properties. Clearly the chemical

composition of the floc is the primary driving force in defining the electrophoretic mobility of the flocs. At high SLES content the flocs would be anticipated to be highly anionic in nature and hence have a high negative electrophoretic mobility. Conversely, at high polymer concentrations (high nitrogen content) it would be anticipated that the flocs would be cationic in nature and hence have a positive electrophoretic mobility.

In addition, it could be anticipated that at a S/N molar ratio of 1 the electrophoretic mobility of the flocs should be approximately zero. If we assume that all nitrogen in the cationic polymer exists in the form of a positively charged quaternary nitrogen then at a S/N molar ratio of 1, each nitrogen would be balanced with an anionic sulphate, as such the floc would be charge neutral. Consequently, the best fit line in Figure 4.26 should pass through the point [1,0]. From Figure 4.26 it can be seen that the best fit line would suggest that charge neutral point is at [0.862,0]. This discrepancy may come from a number of sources, such as experimental error or perhaps more likely, that every nitrogen in the floc is not a positively charged quaternary ion, hence the charge neutral point would be at a lower sulphur content