The Flocculation of Cane Sugar Muds with Acrylamide–Sodium Acrylate Copolymers

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SYNOPSIS

The flocculation of cane sugar muds with commercial acrylamide–sodium acrylate copolymers has been investigated through the measurement of settling rates and residual turbidities. The flocculation efficiencies of the copolymers were observed to depend on their composition, microstructure, and molecular weight, and the zeta potential of the mud particles. Adsorption of polymer at the surface of the particles was shown to occur through interaction with the acrylate groups. The experimental results are consistent with a bridging mechanism for the flocculation process, in which an observed optimum copolymer composition is associated with polymer adsorption which is sufficiently strong to resist mild shear forces yet allows the extension of polymer "loops" and "tails" into solution.

INTRODUCTION

The use of high molecular weight synthetic polymers as flocculants to enhance solid–liquid separations is now common practice in many industrial processes. By far the most common and successful flocculants are polymers consisting of acrylamide and sodium acrylate units. In the Australian raw sugar industry their importance is such that factory operation is now completely dependent on the continuous controlled addition of low doses of these copolymers.

In Australian sugar mills, raw juice at pH 5.5 and 30–35°C is extracted from cane by mechanical crushing. The juice is a solution of sucrose containing both soluble and insoluble impurities. Soluble impurities comprise about 10% of the total dissolved solids and include both organic and inorganic components. Approximately 33% are inorganic, primarily K_2SO_4 with lesser quantities of other salts including Na^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, Cl^-, and other essential plant components. Glucose and fructose represent a further 33% with the remainder being a complex mixture of plant proteins, polysaccharides, amino acids, organic acids, etc. The insoluble impurities are variable in both quantity and type, depending on cane variety, climatic conditions, and field and factory practices. Typically they include minor quantities of starch granules and variable quantities of plant fiber and field soil.

After extraction, the juice is immediately heated to 76 ± 1°C to prevent bacterial degradation of sucrose and to precipitate plant proteins. The pH is then adjusted to 7.5–8.0 by the addition of lime which has been partially or completely dissolved in juice or syrup. This precipitates phosphates as calcium salts so that the juice carries a suspension comprising the original insolubles together with precipitated proteins and phosphates. Despite the complexity of the mixture, Bennett[1] has shown that it behaves electrophoretically as a homogeneous dispersion in which the particle surfaces are characteristically proteinaceous and carry a net negative charge due to the ionization of carboxylic acid groups. The influence of the carboxylic acid groups is greater than expected for a purely proteinaceous surface and Bennett has attributed this to the adsorption of acidic polysaccharides containing more carboxylic groups. After the pH has been adjusted the juice is boiled briefly, polymeric flocculant is added and the insoluble solids separated from clear juice by gravity sedimentation. The clarified juice is subsequently concentrated by evaporation to produce crystalline sucrose.

Despite the importance of polymeric flocculants in the sugar industry and other process industries, no systematic study of the effect of polymer properties on the efficiency of the flocculation reaction has been reported. In this paper we present the results of such an investigation, parts of which have been published previously elsewhere.[2,3]

The majority of colloidal systems of industrial importance contain negatively charged particles. For many, flocculation is most efficiently promoted by the addition of anionic polyelectrolytes based on copolymers of acrylamide and acrylic acid. Flocculation in these systems has generally been attributed to the bridging mechanism which was first suggested by Ruehrwein and Ward.[4] This proposes that segments of individual polymer molecules are adsorbed at the surface of a number of particles so that a three-dimensional network of polymer chains and particles is formed. The resulting aggregates are much larger than the original particles so settling is enhanced. Michaels studied the flocculation of various silts and clays with anionic polyacrylamides. He proposed a bridging mechanism in which polymer adsorption occurs through the acrylamide units of the copolymer and the function of the acrylate units is to expand the polymer molecules so that bridging between particles is more favored.[5] It has also been reported that the adsorption of anionic polyacrylamides by silica and other solids occurs through the amide group.[6-8] The results we report with cane sugar muds are consistent with a bridging mechanism. However they indicate that, in this case, polymer adsorption occurs through the acrylate groups and the latter have no influence on the conformation of the polymer chains.

EXPERIMENTAL

Polymers

An extensive range of commercial acrylamide/acrylic acid copolymers from a number of the major manufacturers was used. In addition, special samples were kindly provided by Allied Colloids Pty. Ltd. and Cyanamid (Australia) Pty. Ltd. The polymers covered the molecular weight range $3-28 \times 10^6$ and their composition varied from 0–60 mol % acrylate.

Copolymer composition was evaluated by elemental analysis of dried samples. The sodium content was determined gravimetrically as sodium sulphate[9] and the nitrogen by the Kjeldahl method.[10] This enabled the molar ratio of the acrylamide to acrylic acid in the copolymer to be calculated. In the

pH range encountered in normal factory operations, the acrylic acid units were completely ionized.

Weight-average molecular weights were determined from viscosity measurements at 30°C in 1 M NaNO$_3$ using the equation $[\eta] = 37.3 \times 10^{-5} M_w^{0.66}$.[11] Klenina and Lebedeva[12] have shown that $[\eta]$ is independent of the degree of hydrolysis for anionic polyacrylamides in solutions of high ionic strength. Polymer (0.1–0.2 g) was added to distilled water (75 cm^3) containing sufficient NaOH (10^{-4} mol) to completely neutralize the acrylic acid units of any of the polymers examined without the risk of inducing further hydrolysis during the time period of the measurements. After stirring gently for 4 h 2 M NaNO$_3$ (100 cm^3) was added and stirring continued for an hour further before diluting to the required concentration. It has been shown that solutions prepared by this procedure reached equilibrium well within this time period. By comparison solutions in which the polymer was added directly to 1 M NaNO$_3$ did not reach equilibrium even after 40 h stirring.[13] Values for $[\eta]$ and the Huggins constant (k) were determined from plots of η_{sp}/C vs. C.

Light scattering measurements were made with a Sofica Model 42000 PGD at 30°C in the presence of NaNO$_3$ and other ions using special perfectly cylindrical glass cells. Solutions were prepared in a manner similar to that used for viscosity measurements. Centrifugation was found to be the most effective procedure for removing dust from polymer solutions since polymer was retained by membrane filters of up to 3.0 μm porosity. Refractive index gradients were measured with a interference refractometer.

^{13}C NMR spectra were recorded on a Bruker AM300 spectrometer. Because of the very high viscosities, solutions of the commercial polymers were prepared directly in the NMR tubes. Polymer powder was rapidly mixed with D$_2$O containing sufficient NaOH to completely neutralize the acrylic acid units. The mixtures were allowed to stand for 48 h then subjected to ultrasonic irradiation for up to 96 h. The viscosities of the resulting gels precluded the use of concentrations greater than $\sim$ 5%. Spectra were recorded at 20°C using a 45° pulse and a pulse delay of 5 sec. Chemical shifts were measured with respect to the resonance of internal p-dioxane taken at 67.40 ppm downfield from TMS.

Electrophoretic Mobilities

The electrophoretic mobilities of cane mud particles were measured at 30°C with a Rank Particle Microelectrophoresis MkII instrument, using reversible

silver/silver chloride electrodes and a flat cell. A laboratory procedure which accurately simulated normal factory operation was used to prepare samples of muds for these experiments. As the particle concentrations were too high for direct observation in the electrophoresis cell, dilution was necessary. The coagulated particles were allowed to settle and the clear supernatant decanted. A few drops of the settled solids were then redispersed in this liquid. Particle numbers were thus reduced to practical levels for observation but the particles were still dispersed in their original liquid phase.

Flocculation Measurements

The settling rates of flocculated muds were measured in a batch test procedure using a perspex fronted timber box in which four calibrated glass settling tubes (45 cm × 5.6 cm diameter) were suspended from perspex inserts. Behind each tube a 45 cm long 53 watt incandescent lamp provided illumination and generated sufficient heat to maintain a temperature close to 100°C within the box. Four 1 L measuring cylinders and four 3 L beakers were set in front of the test apparatus and the required aliquot of 0.1% polymer solution added to each beaker. A large sample (~ 6 L) of juice was obtained from a factory sample point immediately before the clarifier. At this point the juice had been limed, superheated, and flashed to atmosphere so that the sample collected was free of dissolved gases, at a constant temperature of 100°C and constant pH (typically 7.6 ± 0.1). The measuring cylinders were quickly filled and the contents of one cylinder poured into the first beaker. After stirring gently for 10 sec, the flocculated juice was poured carefully into the first settling tube and a stopwatch started. The procedure was repeated with each of the remaining tubes at intervals of 30 sec. The level of the mud interface in each tube was noted at 0.5, 1.0, 2.0, and 3.0 min after filling. For each individual test, the initial settling rate was obtained from a graphical analysis of the data. At the completion of these measurements aliquots of about 20 cm^3 were withdrawn from the supernatants and their absorbance (A) measured at 800 nm in 1 cm glass cells against a distilled water reference. The turbidity of the clarified juice was defined as 100A.

Polymer Adsorption

Early in the research it became evident that the presence of traces of residual flocculant in raw sugar could be detected by a modification of the standard celite filterability test used by Australian raw sugar mills.[14] In this test, the filtration rate of a concentrated sugar solution through a bed of celite filter aid is compared with the rate for a solution of pure sucrose under the same conditions. Filtration rates at pH 7.0 ± 0.1 were observed to be sensitive to the presence of flocculants at the 0.1 ppm level over the full range of compositions used. The filtration test was used as the basis of polymer adsorption studies.

To determine the filterability of a sample juice, about 300 cm^3 collected from the top of a settling tube was centrifuged at 3000g to remove any residual insoluble solids. The supernatant was cooled to 20.0 ± 0.1°C, an aliquot of 200.0 ± 0.1 g weighed out, and the pH adjusted to 7.0 ± 0.1. The solution concentration was measured using a refractometer calibrated for sucrose and sufficient pure sucrose added to increase the concentration to 60.0 ± 0.1% by weight. The solution was stirred for 30 min to dissolve the added sucrose after which 1.15 g of Celite 501 filter aid was added and the solution stirred for an additional 12 min. After standing for 15 min, the filtration rate through a Whatman No. 54 filter paper at a pressure of 345 kPa was measured in standard apparatus. A sample of the original juice was centrifuged and used to prepare standard curves of filterability vs. polymer concentration for each of the flocculants used.

RESULTS AND DISCUSSION

The zeta potentials of a number of cane muds were measured as a function of juice pH at 12 different factories throughout Queensland. It was found that, when the pH was adjusted by the addition of lime in the form of calcium saccharate to simulate normal factory operations, similar results were obtained at factories within a particular region of the industry. However, there were substantial differences between these regions as shown in Figure 1. These may be partly attributed to differences in the phosphate content of the juices of the different regions, since addition of phosphoric acid before liming was shown to reduce the zeta potential of the mud particles. Other factors also probably contribute to the effect. The slight increase in the magnitude of the zeta potential with increasing pH may be due in part to the variation in the degree of dissociation of carboxylic acid groups in polysaccharides adsorbed by the calcium phosphate precipitate, and partly to the effect of pH on the composition of the precipitated calcium phosphate. The low zeta potential values are con-
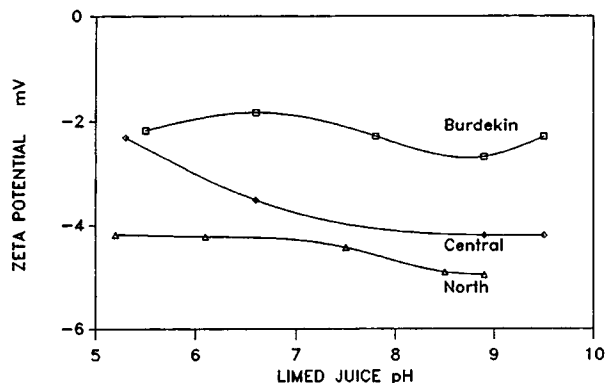
Figure 1   Zeta potential of cane sugar muds as a function of juice pH. Results are given for three Queensland regions.

Figure 2   Effect of solids concentration on settling rate with Superfloc A2120.

sistent with the observation that the particles normally undergo spontaneous rapid coagulation.

Flocculation Studies

In the operation of a sugar factory clarifier, the prime aim is to produce clarified juice of the lowest possible turbidity. At the same time, it is essential to maintain a high rate of sedimentation although not at the expense of any increase in turbidity. These two criteria were therefore used to assess the effectiveness of flocculation.

The influence of solids concentration on settling rates was examined in three series of experiments in which the particle concentration in the juice was varied by adding or withdrawing clear juice prior to the addition of flocculant. In each series, the ratio of polymer to solids was maintained at a constant value and the range of concentrations selected to cover all but the most extreme situations encountered in factory operations. In each case the settling rate decreased as the particle concentration increased, as shown in Figure 2. The particle concentrations in typical Australian cane juices are such that the aggregates formed during flocculation cannot settle independently but interact strongly with other particles. Settling is therefore characterized by a distinct interface between the solids and the clear supernatant. This state is usually described as "hindered settling." In the work described below variations in the absolute values of settling rates were observed which were obviously due to differences in solids concentrations. Rather than attempting to normalize the results to a constant solids concentration, absolute values have been compared only within sets of experiments carried out on single samples of juice.
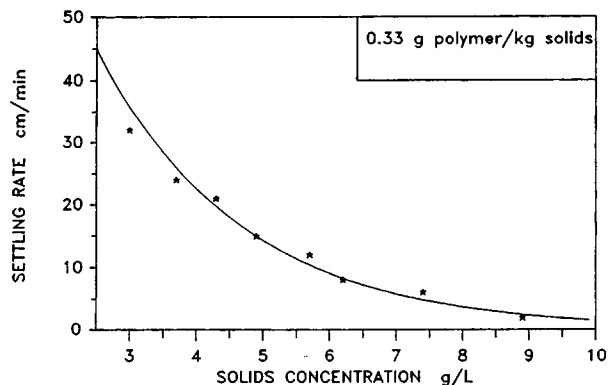
Figure 3 shows the influence of copolymer composition on the settling rates of cane muds measured in factories in the different geographical regions. These results were obtained with a wide range of commercial polymers from a number of manufacturers. However, they were all of similar molecular weight ($10-12 \times 10^6$) and were made by copolymerizing acrylamide and sodium acrylate. In Figure 3 settling rates are expressed as a percentage of the maximum rate observed in each set of experiments. In each region there is a clearly identifiable optimum polymer composition which gives a maximum settling rate. This composition was also found to give clarified juice of minimum turbidity. The optimum polymer composition was determined from curves such as those shown in Figure 3 under various conditions at a number of factories throughout the industry. These results were then compared with zeta potential data obtained at each factory at the same time. Figure 4 shows that the ionic content of the optimum polymer composition increases with the
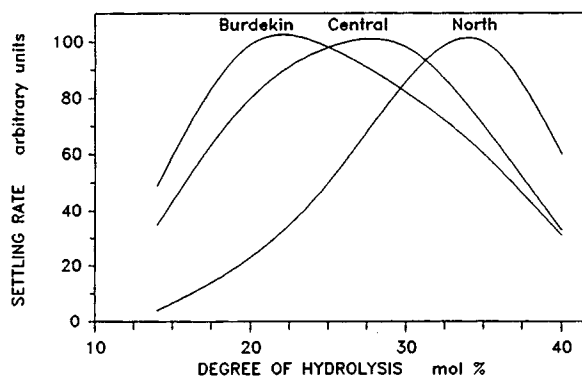
Figure 3   Effect of copolymer composition on settling rates. Results are shown for the same regions as Figure 1.
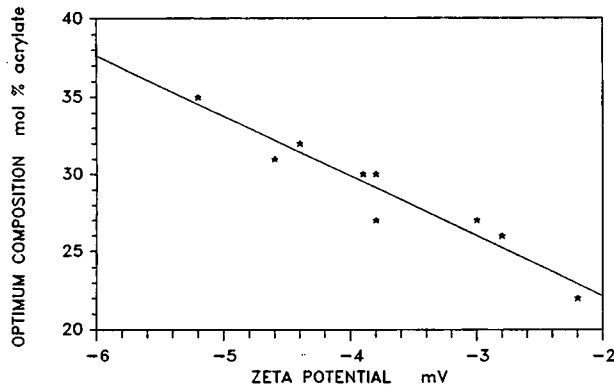
Figure 4 Variation of optimum polymer composition with zeta potential.

zeta potential of the particles. In further experiments with several series of Superfloc polymers covering a wide range of both molecular weight and ionic content, it was observed that an increase in flocculant molecular weight resulted in improvements in both settling rate and turbidity. As illustrated in Figure 5 the ionic content of the optimum polymer composition decreased with increasing molecular weight.

It was also established that polymers synthesized by different methods showed variations in their flocculating abilities. Table I shows data obtained with three commercial polymers of similar molecular weight and composition, one prepared by the polymerization and alkaline hydrolysis of acrylamide, one by the copolymerization of acrylamide and sodium acrylate in aqueous solution, and one by emulsion copolymerization. The polymer prepared by copolymerization hydrolysis was the best flocculant and also had the lowest Huggins constant.

Polymer Adsorption

The adsorption of a range of copolymers was examined in batch settling tests at several factories. Figure 6 shows the results obtained at one factory where the optimum polymer composition for flocculation was 31.4 mol % acrylate. The same general adsorption–composition features were observed at other factories. The results show that polymer adsorption must occur through the ionic acrylate group since the non-ionic polymer is not adsorbed and adsorption increases with the acrylate content of the copolymers. Polymers containing a higher proportion of ionic groups than the optimum polymer composition are almost completely adsorbed. Polymer of optimum composition is approximately 75% adsorbed, although the amount adsorbed increased with continued agitation. Flocculation with the

polymer containing 21.5 mol % acrylate produced some large aggregates and a large number of very small aggregates. In settling experiments, it was observed that the aggregates would continuously break up and reform when subjected to gentle agitation. The amount adsorbed was found to remain constant at about 50%. This is consistent with adsorption being rapid and reversible but not sufficiently strong to resist mild shear forces. With the polymer containing 31.4 mol % acrylate aggregates were visibly much larger, of more uniform size, and were more stable under agitation. In contrast, agitation had no effect on the adsorption of copolymers containing 40 and 48.5 mol % acrylate. This, together with the observed greater stability and smaller size of aggregates formed with these polymers, indicates that adsorption is irreversible in these cases.

The adsorption results are consistent with a bridging mechanism for the flocculation process in which polymer molecules are adsorbed at the surface of particles through the ionic acrylate group. This conclusion is perhaps surprising since it might be expected that electrostatic repulsion would hinder this. As mentioned in the introduction the adsorption of polyacrylamide copolymers to other surfaces has been attributed to interactions involving the amide group of the polymer. It is proposed that in the case of cane mud particles adsorption occurs via a "cation bridge" in which the Ca^{2+} forms a bond between a carboxylate group on the particle surface and another on the polymer. There is evidence in other systems of adsorption occurring through such a bridge.[15-17] Calcium is by far the predominant divalent ion in cane juices and is added in the liming process. With polymers of low acrylate content, adsorption forces are weak and molecules desorb readily. A dynamic equilibrium exists between free and adsorbed molecules and the latter retain their
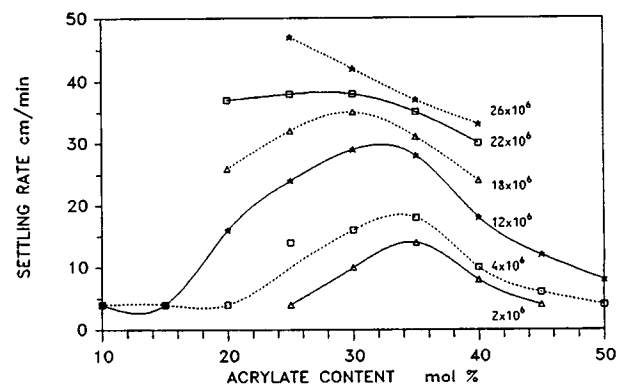
Figure 5 Effect of copolymer composition and molecular weight on settling rates.

**Table I   Effect of Method of Polymer Manufacture on Flocculation Rates**

Polymer	AP273	A130	8025
Method of Manufacture	Hydrolysis	Copolymer	Disperse phase
Ionic Content (mol %)	40	40	39
$10^6 \times M_w$	11.2	10.8	9.8
Huggins Constant	0.22	0.27	0.32
Settling Rate			
Mill A	18	16	8
Mill B	16	11	8
Mill C	27	21	13
Mill D	15	9	6

solution dimensions. Although this state is desirable for segments of polymer molecules to become associated with a number of particles, that is for bridging to occur, the weak adsorption also results in aggregates which are unable to resist even the weak shear forces encountered during settling. With polymer compositions of higher acrylate content than the optimum, adsorption forces are so strong that extended segments of polymer chains are held flat on the surface (trains) and consequently any unadsorbed segments (loops) or chain ends (tails) no longer retain their normal solution dimensions. Bridging between particles is therefore not favored. The optimum polymer composition corresponds to a critical adsorption state between these two extremes, in which polymer segments are held sufficiently strongly to particle surfaces to resist mild shearing forces and yet the polymer loops and tails are still able to retain their normal solution dimensions. This allows adsorbed polymer molecules to sweep up neighboring small particles so that large aggregates result. A similar critical relationship between copolymer composition, energy of adsorption, and the dimensions of the adsorbed molecules has

been predicted by Clayfield and Lumb[18] in mathematical models of copolymer adsorption.

The adsorption of polymer segments of fixed composition is expected to occur to a lesser extent as the surface charge and zeta potential of the particles become more negative, even allowing for Ca^{2+} bridging taking place. In order to attain the critical degree of adsorption required it is necessary to have more adsorption sites. Thus, a copolymer containing a greater proportion of ionic groups is required to maintain optimum conditions for flocculation. With increasing polymer molecular weight more acrylate groups are available through which the adsorption of individual molecules can occur. The critical adsorption state is therefore attained with a copolymer containing a smaller proportion of ionic groups. At the same time the larger effective volume of the adsorbed polymer molecules leads to increased bridging.

The light scattering properties of a number of commercial copolymers were measured in 0.3 mol dm^{-3} $NaNO_3$ in the presence of 5×10^{-3} mol dm^{-3} Ca^{2+}, which approximates to the ionic environment found in cane juice. The combination of the very high molecular weights and the polydispersity of the samples resulted in Zimm plots which were characterized by a distinct curvature in the angular variation of Kc/R, particularly at angles $> 90°$. Although the angular variation was almost linear at low angles, extrapolation to zero angle was achieved by fitting a third order polynomial to the data. The variation with concentration was linear. Table II summarizes values obtained for the radius of gyration, Rg, and shows that, in this environment, Rg does not vary with the acrylate content of the copolymers. It can therefore be concluded that, in the ionic environment experienced in cane juice, electrostatic forces between the ionic groups of the polymers are effectively screened, so that polymer conformation in solution is independent of composition. Thus this factor is not a variable which di-
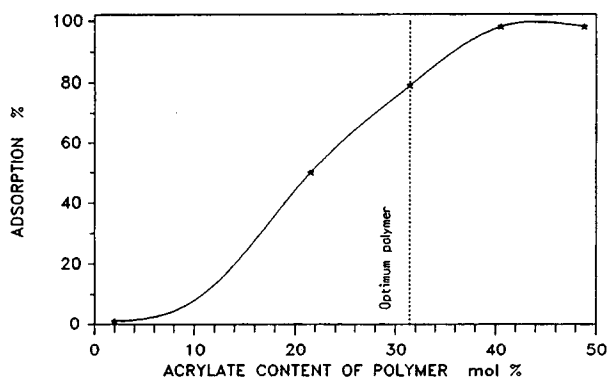
Figure 6   Dependence of polymer adsorption on polymer composition.

rectly influences the flocculation of cane sugar muds. As previously mentioned, the increased expansion of the polymer chains at higher acrylate content has been postulated as promoting bridging between particles in other systems.

Figure 7 shows the ^{13}C-NMR spectra recorded in the carbonyl absorption region for three commercial flocculants. Of these A2115 and A2130 were manufactured by direct copolymerization while XF4282 was manufactured by polymerization and subsequent hydrolysis. XF4282 showed superior flocculating properties to A2130 and had a lower Huggins constant, paralleling the observations reported in Table I for AP273 and A130 respectively. Assignments given in Figure 7 are based on spectra recorded with a range of copolymer compositions of much lower molecular weight, which were synthesized by polymerization and subsequent alkaline hydrolysis of acrylamide. Their ppm values are in reasonable agreement with those found by other workers.[19,20] No peaks were discernible that could be associated with the presence of BBB triads. Comparison of the relative proportion of the four other triad structures present in the copolymers, based on peak area measurements, showed that the data for all copolymers examined conformed substantially more to a Markov statistical model than a Bernoullian one. This is expected since in the copolymerization method of synthesis, electrostatic interactions will inhibit the addition of consecutive acrylate units to a growing chain. Likewise, in the hydrolysis method of manufacture, ionic repulsive forces are expected to protect amide groups from hydrolysis if they are adjacent to acrylate units. Thus random copolymers would not be expected to be formed through either method of synthesis. With the polymers prepared by copolymerization, a best fit to first order Markov statistics resulted when the probability of adding an acrylate unit to a polymer chain terminating in an acrylate unit, was given by 70% of its mole-fraction. With copolymers prepared by hydrolysis the corresponding figure was $\sim$ 50%, indicating that for these polymers the acrylate units occur more frequently adjacent to amide groups. It is suggested that the superior flocculating ability of
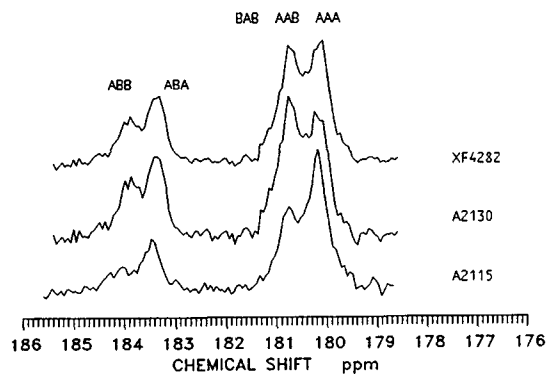
Figure 7 ^{13}C-NMR carbonyl spectra for A2115 (25.8 mol % acrylate), A2130 (40.6 mol % acrylate), and XF4282 (41.0 mol % acrylate).

these polymers is associated with their different microstructure which may have a subtle influence on the interaction of the polymer with Ca^{2+} ions and therefore on polymer adsorption. An identical explanation has been advanced by Truong et al. To account for differences observed in the solubility, in the presence of Ca^{2+}, of sodium acrylate–acrylamide copolymers prepared by copolymerization and hydrolysis.[21] The lower Huggins constant measured for polymers prepared by hydrolysis shows that their microstructure favors stronger polymer–solvent interactions than is the case with polymers prepared by copolymerization. This effect will promote flocculation through the enhancement of interparticle bridging.

In summary the results obtained indicate that flocculation of cane sugar muds by acrylamide–sodium acrylate copolymers proceeds through a bridging mechanism, which is dependent on the adsorption of acrylate groups of the copolymers on the surface of the mud particles. It is likely that this process is facilitated by the presence of Ca^{2+} ions. For optimum flocculation conditions adsorption must be sufficiently strong to withstand mild shear forces, but not too strong to prevent the extension of polymer segments into solution so that maximum interparticle bridging can occur. There is evidence that polymer microstructure can influence flocculation either through its effect on polymer adsorption or polymer–solvent interactions or a combination of these factors.

Table II   Solution Dimensions of Polymers in 0.3 mol dm^{-3} NaNO$_3$ and 5 $\times$ 10^{-3} mol dm^{-3} Ca^{2+}

Polymer	Acrylate/mol %	Rg/nm
A2110	22.8	337 ± 48
A2120	30.8	409 ± 55
A2125	35.5	411 ± 36
A2130	40.6	433 ± 62

REFERENCES

1. M. C. Bennett, *Internat. Sugar J.*, **61**, 77 (1959).
2. O. L. Crees, D. J. Hale, E. Whayman, and A. L. Willersdorf, *Proceedings of the Queensland Society of Sugar Cane Technologists*, **40**, 239 (1973).

3. O. L. Crees, E. Whayman, and A. L. Willersdorf, *Proceedings of the Queensland Society of Sugar Cane Technologists,* **44,** 225 (1977).

4. R. A. Ruehrwein and D. W. Ward, *Soil Sci.,* **73,** 485 (1952).

5. A. S. Michaels, *Ind. Eng. Chem.,* **46,** 1485 (1954).

6. A. P. Black, F. B. Birkner, and J. J. Morgan, *J. Amer. Water Works Assoc.,* **57,** 1547 (1965).

7. O. Griot and J. A. Kitchener, *Trans. Faraday Soc.,* **61,** 1026 (1965).

8. J. V. O'Gorman and J. A. Kitchener, *Inter. J. Mineral Process.,* **1,** 33 (1974).

9. A. I. Vogel, *Quantitative Inorganic Analysis,* Longmans, 1951, p. 482.

10. Standard Method of Test for Total Nitrogen in Resins and Plastics. *American Society for Testing and Materials,* Method No. D1013 (1970).

11. W. A. Barber, *Acrylamide,* American Cyanamid Co., Wayne, NJ (1957).

12. O. V. Klenina and L. G. Lebedeva, *Vysokomol. Soedin. Ser. A.,* **25,** 2053 (1983).

13. O. L. Crees, PhD Thesis, James Cook University of North Queensland (1988).

14. Bureau of Sugar Experiment Stations, *Laboratory Manual for Queensland Sugar Mills,* 5th Ed., Brisbane (1970).

15. A. Sommerauer, D. L. Sussman, and W. Stumm, *Kolloid, Z.,* **225,** 147 (1968).

16. A. Foissy, A. El Attar, and J. M. Lamarche, *J. Colloid Interface Sci.,* **96,** 275 (1983).

17. I. D. Robb and M. Shorples, *J. Colloid Interface Sci.,* **89,** 301 (1982).

18. E. J. Clayfield and E. C. Lumb, *Macromolecules,* **1,** 133 (1968).

19. F. Halverson, J. E. Lancaster, and M. N. O'Connor, *Macromolecules,* **18,** 1139 (1985).

20. H. P. Panzer, F. Halverson, and J. E. Lancaster, *Polym. Mater. Sci. Eng.,* **51,** 268 (1984).

21. D. N. Truong, J. C. Galin, J. Francois, and Q. T. Pham, *Polym. Communications,* **25,** 208 (1984).