

# Highly Concentrated Cationic Flocculants Based on 80/20 wt % [2-(Acryloyloxy)ethyl]trimethylammonium Chloride/Acrylamide in an Inverse Microemulsion: Influence of the Copolymerization Variables on the Flocculation Performance

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**ABSTRACT:** The influence of the total comonomer concentration (TCC; 30–42 wt %), emulsifier concentration (EC; 7.3–23 wt %), hydrophilic–lipophilic balance (HLB; 9–9.9), crosslinking agent (*N,N'*-methylene bisacrylamide) concentration (CAC; 0–122.8 ppm with respect to TCC), and isopropyl alcohol (chain-transfer agent) concentration (IPC; 0–1.5 wt % with respect to TCC) on the flocculation performance (FP) of 80/20 wt % acrylamide (AM)/[2-(acryloyloxy)ethyl]trimethylammonium chloride (ADQUAT) copolymers obtained by semicontinuous inverse microemulsion copolymerization was studied with capillary suction time testing for FP assessment on anaerobic digested sludges. FP increased as TCC decreased, was nearly unaffected by EC, was maximum with an HLB of 9.5, decreased strongly with CAC, and showed a peak value with an IPC of 1 wt %. At a very high TCC, copolymer growth in a highly collapsed state resulted in greatly structured, high

weight-average molar mass flocculants with decreased swelling capacities (SCs), which did not favor bridging flocculation, and in increased shielding of their positive charges, which did not favor charge neutralization flocculation. However, industrially needed latices with both high TCC and good FP could be obtained by the addition of isopropyl alcohol, which, below a concentration of 1 wt %, improved FP by decreasing the weight-average molar mass and thereby enhancing SC while maintaining long enough chains to be effective for bridging flocculation. On the basis of the results, new star-shaped ADQUAT/AM copolymers are envisioned as flocculants with superior FP. A synthetic route is proposed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3132–3142, 2009

**Key words:** hydrophilic polymers; polyelectrolytes; star polymers; water-soluble polymers

## INTRODUCTION

Acrylamide (AM)-based, water-soluble, cationic copolymers are highly demanded industrial materials because of their various applications, such as flocculants in wastewater treatment, antistatic agents

for textile treatment, and solid retention agents in paper making.<sup>1</sup> One of the more industrially important families of AM-based cationic flocculants consists of copolymers of AM and [2-(acryloyloxy)ethyl]trimethylammonium chloride (ADQUAT) with different ADQUAT/AM ratios. Generally, high-molecular-weight copolymers are desired for the aforementioned applications. However, the handling of these products in their solid form is not easy because of their hygroscopic character and because they are difficult to dissolve. On the other hand, their concentrated aqueous solutions are also difficult to handle because of their high viscosities. Additionally, the cationic copolymers degrade continuously in aqueous solutions. To avoid these constraints, inverse emulsion copolymerization is broadly used.<sup>2</sup> This method involves the

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copolymerization of an aqueous comonomer solution dispersed in a continuous organic phase, which results in a copolymer inverse emulsion. However, although inverse emulsion latex particles are easy to handle and can be obtained with copolymer concentrations above 30 wt % with emulsifier concentrations (ECs) below 4 wt % (with respect to the total emulsion weight), they lack thermodynamic stability, and this results in phase separation.

To overcome this problem, during the 1980s, a new polymerization method was used to obtain these products: inverse microemulsion polymerization.<sup>3</sup> Microemulsions are transparent, homogeneous mixtures of water (or an aqueous solution of chemicals) and oil stabilized by a fairly large amount of a surfactant or, in most cases, a surfactant mixture. Unlike emulsions, microemulsions are thermodynamically stable. The inverse microemulsion copolymerization of AM and ionic monomers allows the preparation of stable, clear or milky, low-viscosity microlatex particles of a high molar mass ( $\sim 10^7$  g/mol). However, to achieve this goal, a higher concentration of a surfactant mixture must be used in comparison with inverse emulsions to stabilize the system. EC in an inverse emulsion ranges from 2 to 4 wt %; this is considerably lower than EC in inverse microemulsions, which is generally  $>10$  wt %, although lower concentrations are needed if a heterophase water-in-oil polymerization process is used,<sup>4</sup> by means of which, starting from an inverse emulsion of monomers, an inverse microemulsion is obtained after polymerization.

Nevertheless, as far as we know, the lower ECs reported for inverse microemulsions of ADQUAT/AM copolymers range from 7 to 9 wt % with ADQUAT/AM ratios of 60/40<sup>5,6</sup> and 40/60,<sup>7,8</sup> respectively; these ECs are much higher than those used for inverse emulsions.

To reduce EC as much as possible is a continuous necessity for both environmental and economic reasons. Up to now, attempts at reducing EC below the aforementioned levels have been unsuccessful, resulting in phase separation during or after polymerization. Then, an alternative is to obtain latices with much higher copolymer concentrations than those currently reported in the literature, which are lower than 25 wt % for both polyacrylamide inverse microemulsions<sup>4,8-13</sup> and AM-based anionic and cationic copolymer inverse microemulsions.<sup>14-19</sup>

We achieved higher polymer contents for ADQUAT/AM copolymers with ADQUAT/AM weight ratios of 60/40<sup>5,6</sup> and 40/60,<sup>7,8</sup> in which the total copolymer concentrations were between 28 and 34.5 wt %, and, recently, for ADQUAT/AM copolymers with an ADQUAT/AM weight ratio of 80/20,<sup>20</sup> in which the total copolymer concentrations ranged from 30 to 42.0 wt %. In the last study, the

semicontinuous inverse microemulsion copolymerization of 80/20 wt % (59.5/40.5 mol %) ADQUAT/AM in an isoparaffinic solvent, Isopar M, with high total comonomer concentrations (TCCs; 30–42 wt %) was examined with a mixture of nonionic surfactants [Crill 43, a sorbitan sesquioleate with a hydrophilic-lipophilic balance (HLB) of 3.7, and Softanol 90, a C<sub>11</sub>–C<sub>13</sub> secondary ethoxylated fatty alcohol with an HLB of 13.3] as the emulsifier and sodium metabisulfite as the initiator; the influence of copolymerization parameters, such as TCC, EC, HLB, the isopropyl alcohol (chain-transfer agent) concentration (IPC), and the crosslinking agent (*N,N'*-methylene-bis-acrylamide) concentration (CAC), on the weight-average molar masses ( $M_w$ 's), viscosities in aqueous solutions, and structuring degrees [viscometric structuring index (VSI)] of the obtained copolymers was analyzed.

In this article, the influence of the same copolymerization variables on the flocculation performance (FP) of the aforementioned inverse microemulsions of 80/20 wt % (59.5/40.5 mol %) ADQUAT/AM copolymers is studied, with FP being correlated with the  $M_w$  and VSI values of cationic copolymers.

## EXPERIMENTAL

### Materials

The synthesis of the inverse microemulsion samples herein used (hereafter simply called samples) and the influence of the copolymerization variables on the copolymer properties ( $M_w$ , viscosity, and VSI) have been reported elsewhere.<sup>20</sup> Inverse microemulsions of 80/20 wt % ADQUAT/AM copolymers were prepared by the semicontinuous inverse microemulsion copolymerization of a 80/20 wt % ADQUAT/AM mixture in an isoparaffinic solvent, Isopar M, with a mixture of nonionic surfactants [Crill 43, a sorbitan sesquioleate with an HLB of 3.7 supplied by Croda (East Yorkshire, United Kingdom), and Softanol 90, a C<sub>11</sub>–C<sub>13</sub> secondary ethoxylated fatty alcohol with an HLB of 13.3 supplied by Quimidroga (Barcelona, Spain)] as the emulsifier and sodium metabisulfite as the initiator.

### Copolymer characterization

The  $M_w$ , absolute viscosity (BV; i.e., the viscosity of a 0.5 g/L aqueous solution of a copolymer in demineralized water type I), and standard viscosity (SV; i.e., the viscosity of a 0.5 g/L aqueous solution of a copolymer in 0.005M NaCl in demineralized water type I) values were determined with equipment and procedures described in ref. 20.

The BV/SV ratio is an index of the structuring degree of a copolymer,<sup>21</sup> and in this article, it is called VSI. The higher VSI is, the higher the copolymer

TABLE I  
Sample Characteristics

Sample	TCC (wt %)	EC (wt %)	HLB	IPC (wt %)	CAC (ppm)	BV (cP)	SV (cP)	VSI	$M_w \times 10^{-6}$ (g/mol)
1	30.0	7.3	9.5	0	0	110.0	29.4	3.7	4.83
2	33.5	7.3	9.5	0	0	158.2	33.0	4.8	5.84
3	37.5	7.3	9.5	0	0	181.8	36.2	5.0	6.24
4	42.0	7.3	9.5	0	0	177.4	30.4	5.8	9.33
5	42.0	10	9.5	0	0	149.6	33.6	4.5	9.89
6	42.0	13	9.5	0	0	156.0	34.2	4.5	4.13
7	42.0	7.3	9	0	0	138	27.8	5.0	6.77
8	42.0	7.3	9.9	0	0	200.2	31.1	6.4	9.54
4-bis <sup>a</sup>	42.0	7.3	9.5	0	0	161.4	33.2	4.9	8.89
9	42.0	7.3	9.5	0.5	0	142.0	32.4	4.4	6.34
10	42.0	7.3	9.5	0.75	0	134.2	25.8	5.2	7.39
11	42.0	7.3	9.5	1.0	0	128.6	23.2	5.5	5.89
12	42.0	7.3	9.5	1.5	0	128.0	23.6	5.4	2.21
13	42.0	7.3	9.5	0	10.0	>200 <sup>b</sup>	16 <sup>b</sup>	>12.5	–
14	42.0	7.3	9.5	0	30.0	182.4	7.2 <sup>b</sup>	25.3	–
15	42.0	7.3	9.5	0	62.2	157.0	3.0 <sup>b</sup>	52.3	–
16	42.0	7.3	9.5	0	122.8	169.0	2.4 <sup>b</sup>	70.4	–

TCC and EC are based on the total inverse microemulsion amount; IPC and CAC are based on the total comonomer amount (the crosslinking agent was MBA).

<sup>a</sup> Run 4-bis was run 4 repeated. It was necessary for comparison because the ADQUAT monomer used from run 9 to run 16 came from another manufacturing batch, so its reactivity was different. This explains the difference in the results obtained for the two runs.

<sup>b</sup> These values are outside the recommended viscometer measurement range (20–200 cP). The viscosity accuracy was  $\pm 2\%$  for the rest of the samples.

structuring degree is. In this article, the term *structuring* encompasses branching and crosslinking.

### Flocculation tests

FP of the cationic copolymers was analyzed through the measurement of the capillary suction time (CST) with a 304B capillary suction timer from Triton Electronics, Ltd. (Dunmow, United Kingdom). The test<sup>22</sup> was performed by the treatment of sludge with a dose of a flocculant and then the placement of the sludge in an upright metallic cylinder, or sludge reservoir, resting on standard filter paper (CST paper,  $7 \times 8 \text{ cm}^2$ , Triton Electronics). The capillary suction of the paper extracted liquid from the sludge, wetting the paper. The time required for the filtrate to flow 1 cm radially was recorded as the CST. The lower CST is, the higher the copolymer FP is. CST is a method that measures the filtration rate and is used for characterizing sludge filterability and conditionability. Sludge filterability governs predominantly the output of nearly all dewatering equipment, including drying beds, belt presses, vacuum filters, filter presses, and centrifuges. However, CST gives no information about the floc strength, a very important parameter for forming robust flocs well suited to high-shear applications such as centrifugation.

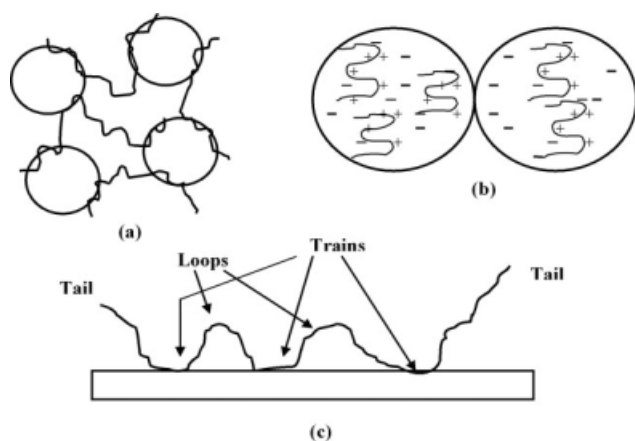
For the flocculant dosage, a diluted solution of a sample (1 g/L) was prepared directly by the inver-

sion of the sample as it was synthesized over stirred water at room temperature. After 15 min, the solution was ready to be used. For each test series, 100 g of fresh, homogenized, and tempered sludge was poured into a beaker. Then, a specific dose of the copolymer solution was quickly added by means of a syringe. The mixture was stirred at 1000 rpm for 60 s with a Triton WRC type 131 stirrer timer (Triton Electronics). Afterwards, an aliquot was poured into the sludge reservoir of the CST equipment, and CST was recorded. To compare FP for different samples, the CST values were plotted against the copolymer (active matter) dosage.

The sludges were anaerobically digested and were obtained from the Vitoria Municipal Water Treatment Plant (Vitoria, Spain). Sludge S1 (pH = 7.4, solid concentration = 3.5 wt %) was used for studying the influence of the TCC, EC, and emulsifier HLB values. Sludge S2 (pH = 7.1, solid concentration = 5.3 wt %) and sludge S3 (pH = 6.6, solid concentration = 7.4 wt %) were used for studying the influence of IPC and CAC, respectively.

## RESULTS AND DISCUSSION

The characteristics of the samples and the properties ( $M_w$ , BV, SV, and VSI) of the corresponding cationic copolymers are given in Table I.



**Figure 1** Flocculation mechanisms: (a) bridging, (b) electrostatic patch, and (c) types of polymeric segments adsorbed on a particle surface.

### Flocculation mechanisms

Generally accepted flocculation theory involves basically two action mechanisms:<sup>23</sup>

- Polymer bridging [Fig. 1(a)]. The first step is the adsorption of the macromolecular chain onto the surface of a particle to be flocculated, and the second one is polymer bridging, in which the polyelectrolyte adsorbed onto that particle has looped and dangling chains extending some way into the solution that can attach to nearby particles, resulting in large flocs and accelerated rates of sedimentation. This mechanism is favored by linear, high-molecular-mass flocculants, and for polyelectrolytes, there is an optimum charge density on the macromolecular chain above which the charge sign on the particle surface is inverted and electrostatic repulsion between particles is produced, preventing polymer bridging action. Flocculation depends on the adsorption structure and conformation of the ionic polymer. Cationic flocculants bind to the particle surface in different conformations [Fig. 1(b)]: trains, in which polymer segments are adsorbed in a flat configuration; tails, in which polymer segments are projected into the solution from the particle surface; and loops, in which a polymer segment forms a loop between two trains.
- Charge neutralization. The macromolecular chain is adsorbed onto the oppositely charged particle surface as a result of strong electrostatic attraction. Therefore, flocculation could occur simply as a result of the reduced surface charge of the particles, leading to decreased electrical repulsion between them. Ionically charged flocculants are desired for enhancing the adsorption charge neutralization action. In this case, there

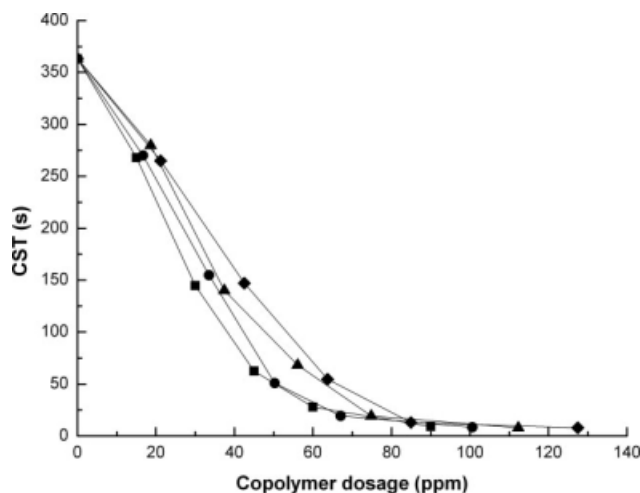
is little, if any, opportunity for bridging interactions. However, in many practical cases, particles are negatively charged. Then, for highly charged cationic polyelectrolytes and particles with weakly charged negative surfaces, another variation of this mechanism is the electrostatic patch [Fig. 1(c)], by which the cationic polyelectrolyte will basically adsorb onto the particles in a rather flat configuration. Consequently, although the overall charge of particle surfaces is close to neutrality, it is physically impossible for each surface-charged site to be neutralized by a cationic polymer segment because the average distance between surface sites is greater than that between charged segments along the macromolecular chain. As a result, there are patches of positive charge between zones of unadsorbed negatively charged surface. Then, domains oppositely charged in adjacent particles will combine, resulting in agglomeration, that is, in larger flocs and consequently in enhanced flocculation. Flocs thus produced are stronger than ones formed by simple charge neutralization.

The flocculants herein studied all have the same cationic charge; consequently, it is to be expected that the bridging mechanism will govern FP of the samples herein reported, even though the charge neutralization mechanism depends not only on the ionic charge but also on the ionic charge distribution along the macromolecular chain.

### Influence of TCC

The influence of TCC (weight percentage based on the total mass of the microemulsion) on FP, as measured by CST with an HLB of 9.5 and an EC of 7.3 wt %, was studied with samples 1–4 (Table I) and sludge S1. The results are plotted in Figure 2.

As can be seen, FP decreases as follows: 30 wt % TCC  $\sim$  33.5 wt % TCC > 37.5 wt % TCC > 42 wt % TCC. At first, this behavior seems anomalous because  $M_w$  increases dramatically with TCC and so FP should increase with TCC according to the bridging flocculation mechanism. However, as discussed by Ochoa-Gómez et al.,<sup>20</sup> latex particles are smaller than copolymer radii of gyration; this means that copolymer chains grow in a highly collapsed state, which leads to copolymer branching and crosslinking by the two mechanisms discussed in that article. Therefore,  $M_w$  increases with TCC because of the increasingly structured nature of the copolymer chains as TCC increases; this is reflected by the VSI parameter, which measures the copolymer structuring degree.



**Figure 2** Variation of CST as a function of the copolymer dosage for several TCCs: (■) 30, (●) 33.5, (▲) 37.5, and (◆) 42 wt % (HLB = 9.5, EC = 7.3 wt %, IPC = 0 wt %, CAC = 0 ppm).

As can be seen in Table I, VSI increases from 3.7 (at TCC = 30 wt %) to 5.8 (at TCC = 42 wt %); that is, a comonomer concentration increase of 40% causes an increase of 56.7% in VSI. The structured nature of the copolymers obtained at high TCCs leads to a decrease in their swelling capacities in aqueous solutions, which does not favor flocculation by the bridging mechanism, and also to a shielding of their positive charges, which does not favor charge neutralization flocculation. Consequently, FP decreases with TCC, despite the high increase in  $M_w$  with TCC.

It is worth mentioning that the required properties of a flocculant depends on the solid to be flocculated. Although linear, high-molecular-mass flocculants are generally preferred, in some applications, structured flocculants are required;<sup>24–26</sup> therefore, inverse microemulsion polymerization at high monomer concentrations is a suitable procedure for obtaining them.

### Influence of EC

The influence of EC (weight percentage based on the total mass of the microemulsion) on FP, as measured by CST with an HLB of 9.5 and a TCC of 42.0 wt %, was studied with samples 4–6 (Table I) and sludge S1. The results are plotted in Figure 3.

As can be seen, FP is as follows: 13 wt % EC = 7.3 wt % EC  $\sim$  10 wt % EC. In the range of ECs studied, the influence of EC on FP is very slight, if there is any. On the one hand, as TCC is constant, an increase in EC causes an increase in the number of micelles. Therefore, the number of comonomer molecules per micelle decreases, and consequently, the probability of transfer to both radically active surfac-

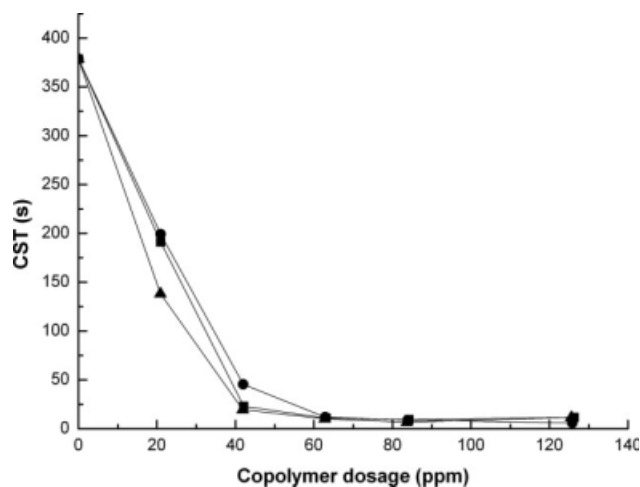
tant<sup>27</sup> and other growing copolymer chains is lower; this leads to less structured copolymers, as confirmed by the variation of VSI with EC. A less structured copolymer has a higher swelling capacity in an aqueous solution, which favors flocculation by the bridging mechanism. On the other hand, the size of latex particles decreases as EC increases.<sup>10,11,16</sup>

Accordingly, the higher EC is, the higher the surface area (area/volume ratio) is of micelles; therefore, there is a larger area available for initiator diffusion from the oil phase to water pools inside micelles. Consequently, the number of initiator molecules that enter micelles per unit of time is higher, and this reduces the comonomer/initiator concentration ratio, resulting in lower  $M_w$  values in comparison with those obtained at lower ECs. A lower  $M_w$  value means a lower flocculation capacity by particle bridging and also by charge neutralization because of the lower capacity for particle surface coverage. Consequently, the positive influence on FP as VSI decreases with EC is counteracted by a negative influence as  $M_w$  decreases with EC, and EC has practically no influence on FP under the experimental conditions studied.

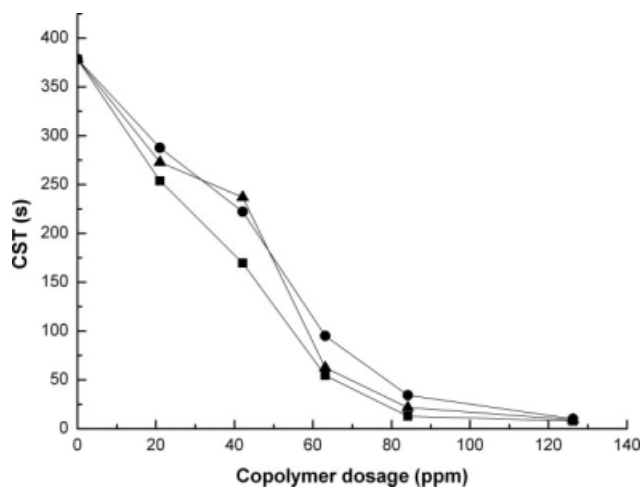
### Influence of HLB

The influence of HLB on FP as measured by CST with a TCC of 42.0 wt % and an EC of 7.3 wt % was studied with samples 4, 7, and 8 in Table I and sludge S1. The results are plotted in Figure 4. As can be seen, FP is as follows: HLB = 9.5 > HLB = 9.9  $\gg$  HLB = 9.0.

The influence of HLB on FP can be divided in two HLB intervals:



**Figure 3** Variation of CST as a function of the copolymer dosage for several ECs: (■) 7.3, (●) 10, and (▲) 13 wt % (HLB = 9.5, TCC = 42 wt %, IPC = 0 wt %, CAC = 0 ppm).



**Figure 4** Variation of CST as a function of the copolymer dosage for several HLBs: (■) 9.5, (●) 9.0, and (▲) 9.9 (TCC = 42 wt %, EC = 7.3 wt %, IPC = 0 wt %, CAC = 0 ppm).

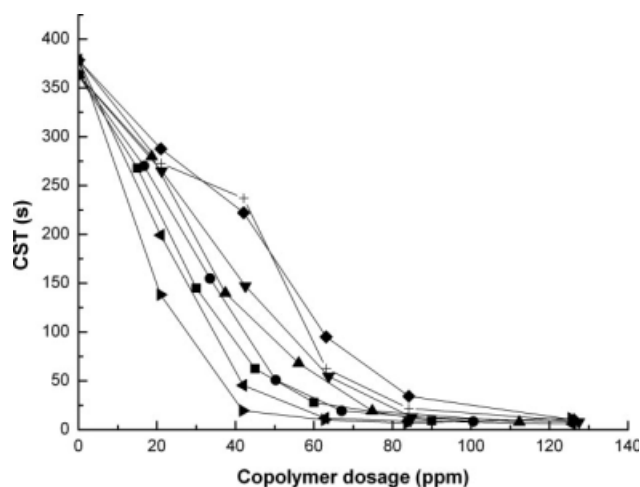
- HLB range of 9–9.5. In this range, FP increases with HLB. Both  $M_w$  and VSI increase with HLB, but, although VSI increases only by 16%, BV, which is an indirect measurement of the copolymer swelling capacity in solution, and  $M_w$  increase by 28.5% and 37.8%, respectively. The percentage increase in VSI is much lower than the corresponding increases in  $M_w$  and BV. This suggests, on the one hand, that copolymer structuring can be mainly attributed to branching and not to crosslinking because crosslinking reduces the copolymer swelling capacity and then its BV in aqueous solutions, whereas branching does not necessarily have the same effect; on the other hand, the branching number per macromolecular chain does not increase significantly in comparison with  $M_w$ , and so the linearity of copolymer chains is only slightly reduced from an HLB of 9 to an HLB of 9.5. As a result, when the copolymerization HLB is shifted from 9 to 9.5, cationic flocculants with longer chains and greater swelling capacities are obtained, and this results in higher FP because both features favor flocculation by the bridging mechanism.
- HLB range of 9.5–9.9. In this range, FP decreases slightly with HLB.  $M_w$  increases by 2.2%, VSI increases by 10.3%, and BV increases by 12.8%; this means that more structured flocculants have been obtained in comparison with the aforementioned HLB interval.  $M_w$  hardly varies with HLB, but VSI increases, and this indicates that more branched copolymers are obtained. However, the VSI increment, which does not favor flocculation by bridging action, is not high, and it is of the same order as the BV increment, which favors flocculation by the

bridging mechanism. Consequently, the respective influences of both parameters on FP are counteracted, and this leads to a slight decrease in FP with HLB.

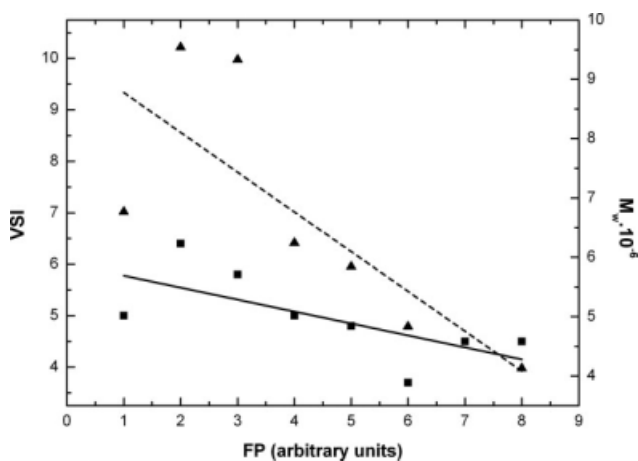
### Correlation between FP and copolymer properties (VSI and $M_w$ )

The variation of CST as a function of the copolymer dosage for samples 1–8 is plotted in Figure 5 (sludge S1). On the basis of this figure, an FP score ranging from 1 (worst FP: the sample with higher CST values) to 8 (best FP: the sample with lower CST values) can be assigned to every sample: (1) sample 7, (2) sample 8, (3) sample 4, (4) sample 3, (5) sample 2, (6) sample 1, (7) sample 5, and (8) sample 6. Thereafter, a correlation between the copolymer properties and FP can be obtained through the plotting of  $M_w$  and VSI against the FP score, as depicted in Figure 6.  $M_w$  from run 5 has not been included because it deviates strongly from the general pattern observed in the figure.

Correlation coefficients are in both cases lower than 0.5, indicating that there is not a linear relationship between the parameters and FP; this was expected because FP also depends on other polymer characteristics not studied here, such as the copolymer microstructure (the charge distribution and comonomer sequence distribution in the copolymer).<sup>28</sup> The different samples used could be composed of copolymers with different microstructures as a result of a composition drift during copolymerization due to differences in the comonomer reactivities. Because the comonomer conversions were very close to 100% for all samples herein used,<sup>20</sup> the average compositions were obviously the same for all



**Figure 5** Variation of CST as a function of the copolymer dosage for samples 1–8: (■) 1, (●) 2, (▲) 3, (▼) 4, (◄) 5, (►) 6, (◆) 7, and (+) 8.



**Figure 6** Plots of (■, —) VSI and (▲, - - -)  $M_w$  versus FP for samples 1–8.

samples (80 : 20 wt % ADQUAT/AM). However, differences in the composition polydispersities between samples of the same average composition would involve the coexistence of polyelectrolytes with different cationic charges inside the same microlatex and, therefore, with different properties, such as different FPs.

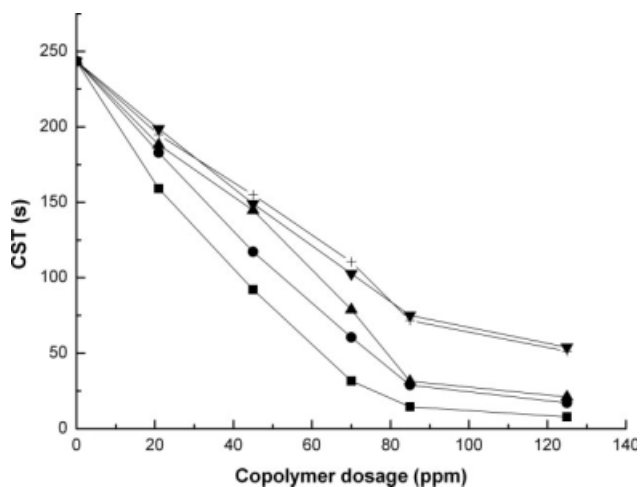
Lacík et al.<sup>29</sup> demonstrated the strong influence of compositional heterogeneity due to the composition drift during polymerization on the rheological properties of water-soluble polymers, and Sasia et al.<sup>7</sup> reported a strong average copolymer composition drift with conversion for a system very similar to the one herein studied, 40 : 60 wt % ADQUAT/AM, from 57 wt % ADQUAT at a conversion of 60% to 40 wt % ADQUAT at a conversion close to 100%. This means that the copolymer composition at low conversions could be very close to 100 wt % ADQUAT. Consequently, in the earlier steps of copolymerization, poly[[2-(acryloyloxy)ethyl]trimethylammonium chloride} homopolymers would be the only species formed, and copolymers with different and decreasing ADQUAT compositions would be obtained as copolymerization proceeded. Even at the end of copolymerization, uncharged polyacrylamide homopolymers could be obtained, and these are not useful for sludge dewatering. Of course, the relative distribution (composition polydispersity) of these differently charged macromolecules may vary as the experimental copolymerization conditions change from sample to sample, and this has an influence on FP and also on rheological properties.

Taking into account the previous discussion, we find that the probability of the samples herein studied being comprised of copolymers with different microstructures is high, and this has led to the dispersion of data observed in the relationships presented in Figure 6. Despite this, the general variation pattern clearly shows that FP decreases as both VSI

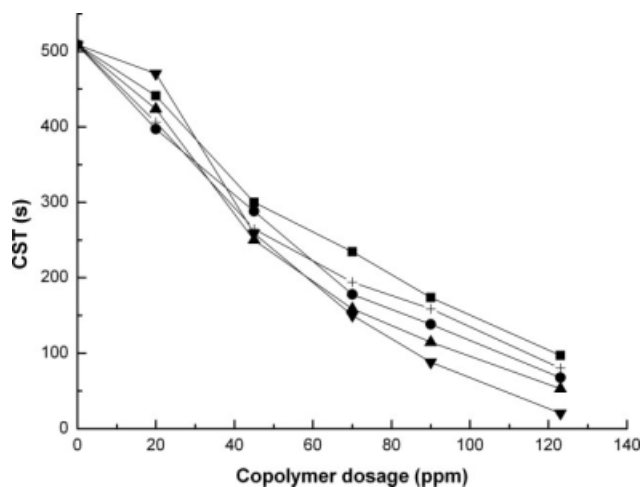
and  $M_w$  increase. This means that the best FPs are obtained with less structured copolymers with not too long chains.

The negative influence of the structuration degree on FP was definitely confirmed by an analysis of the influence of *N,N'*-methylene bisacrylamide as a crosslinking agent on FP, which was studied with a TCC of 42.0 wt %, an HLB of 9.5, and an EC of 7.3 wt % with samples 4-bis and 13–16 (Table I) and sludge S3 (fresh sludge was used instead of the older sludges S1 and S2 for reasons specified previously). The results are plotted in Figure 7. As can be seen, the FP variation is as follows: 0 ppm CAC > 10 ppm CAC > 30 ppm CAC >>> 62.2–122.8 ppm CAC. Because VSI increases with CAC and in the range studied there is practically a linear relationship (correlation coefficient = 0.95) between them, the decline of FP with CAC can be attributed to the increase in VSI, which can be explained if we take into account that crosslinking results in copolymers with a lower swelling capacity in aqueous solutions, as indicated by the decrease in BV with TCC above a CAC of 10 ppm, which does not favor particle bridging flocculation, and also in copolymers with a higher shielding degree of their positive charges, which does not favor charge neutralization flocculation.

In summary, the results reported up to now show clearly that inverse microemulsion copolymerization at a high TCC leads to structured copolymers, and the higher TCC is, the higher the structuring degree is. Likewise, as demonstrated by Ochoa-Gómez et al.,<sup>20</sup> by means of this copolymerization technique, it is possible to obtain very high molecular mass ADQUAT/AM copolymers only by increasing for a time their structuring degree, that is, by branching



**Figure 7** Variation of CST as a function of the copolymer dosage for several CACs: (■) 0, (●) 10, (▲) 30, (▼) 62.2, and (+) 122.8 ppm (HLB = 9.5, TCC = 42.0 wt %, EC = 7.3 wt %, IPC = 0 wt %).



**Figure 8** Variation of CST as a function of the copolymer dosage for several IPCs with a TCC of 42 wt %: (■) 0, (●) 0.5, (▲) 0.75, (▼) 1.0, and (+) 1.5 wt % (HLB = 9.5, EC = 7.3 wt %, CAC = 0 ppm).

and/or crosslinking. In fact, for samples 1–8, there is a linear relationship between  $M_w$  and VSI with a correlation coefficient of 0.83, which is low for justifying a perfectly linear relationship between the two parameters but high enough for accepting that it exists, mainly because all samples were obtained under very different experimental conditions. Therefore, it is not possible to obtain linear, very high molecular mass copolymers with inverse microemulsion copolymerization at a high TCC. Under these circumstances, FP is negatively affected because copolymers obtained at a high TCC grow in a highly collapsed state in comparison with those at a low TCC, and this results in a higher structuration degree and hence in lower FP.

However, microemulsions with both high flocculant concentrations and good FP are industrially demanded. If we take into account the previous discussion, this can be envisioned only by copolymerization in the presence of a structuring-control agent such as a chain-transfer agent. Consequently, several experiments were carried out to study the influence on FP of isopropyl alcohol, a well-known chain-transfer agent, with a TCC of 42 wt %. The results are reported in the next section.

### Influence of IPC

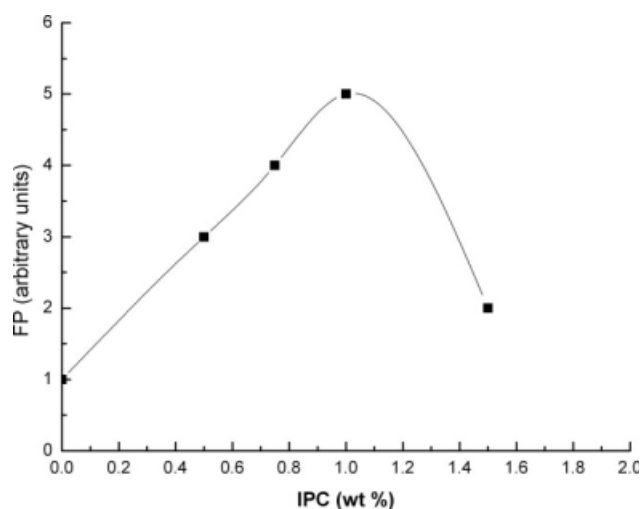
The influence of IPC (weight percentage based on the total comonomer content) on FP, as measured by CST with a TCC of 42.0 wt %, an EC of 7.3 wt %, and an HLB of 9.5, was analyzed with samples 4-bis and 9–12 (Table I). Fresh sludge (S2) from the same municipal water treatment plant was used instead of sludge S1 because preliminary experiments showed that absolute FP depends on the sludge storage time:

FP is constant only if the sludge storage time is less than 7 days.

The results are plotted in Figure 8. FP is as follows: 1.0 wt % IPC > 0.75 wt % IPC > 0.5 wt % IPC > 1.5 wt % IPC > 0 wt % IPC. By assigning an arbitrary FP score ranging from 1 (worst FP: the sample with higher CST values) to 5 (better FP: the sample with lower CST values), we obtained the relationship between FP and IPC plotted in Figure 9.

As can be seen from Figures 8 and 9, the behavior predicted in the previous section is accomplished up to an IPC of 1 wt %: FP increases with IPC. Then, FP decreases dramatically, although it is still slightly better at an IPC of 1.5 wt % than at an IPC of 0 wt %. Up to an IPC of 0.5 wt %, both VSI and  $M_w$  decrease, and this indicates that less structured copolymers with sufficiently high  $M_w$  values are obtained, resulting in copolymers with better flocculation properties. Therefore, isopropyl alcohol behaves as a chain-transfer agent, as expected.

However, between IPCs of 0.5 and 0.75 wt %, both VSI and  $M_w$  increase; however, although VSI is 6.1% higher than at an IPC of 0 wt %,  $M_w$  is still 17.9% lower than  $M_w$  for the same sample. This means that in addition to its chain-transfer action, as indicated by the  $M_w$  reduction with respect to the sample with an IPC of 0 wt %, more than 0.5 wt % isopropyl alcohol induces some structuring degree in the macromolecular chains, which leads to an increase in  $M_w$  from an IPC of 0.5 wt % to an IPC of 0.75 wt %. The VSI values are much lower than those obtained by the introduction of the crosslinking agent *N,N'*-methylene-bis-acrylamide (see samples 13–16 in Table I), and this suggests that structuring induced by isopropyl alcohol is mainly due to branching. On the other hand, the slight increase in VSI indicates that



**Figure 9** Variation of FP with IPC (weight percentage based on TCC; TCC = 42.0 wt %, EC = 7.3 wt %, HLB = 9.5).



copolymer chains are being structured by the introduction of short-chain branching, probably because, on account of the high comonomer concentration, once a branch starts to grow, the probability of transfer to the comonomers is very high.

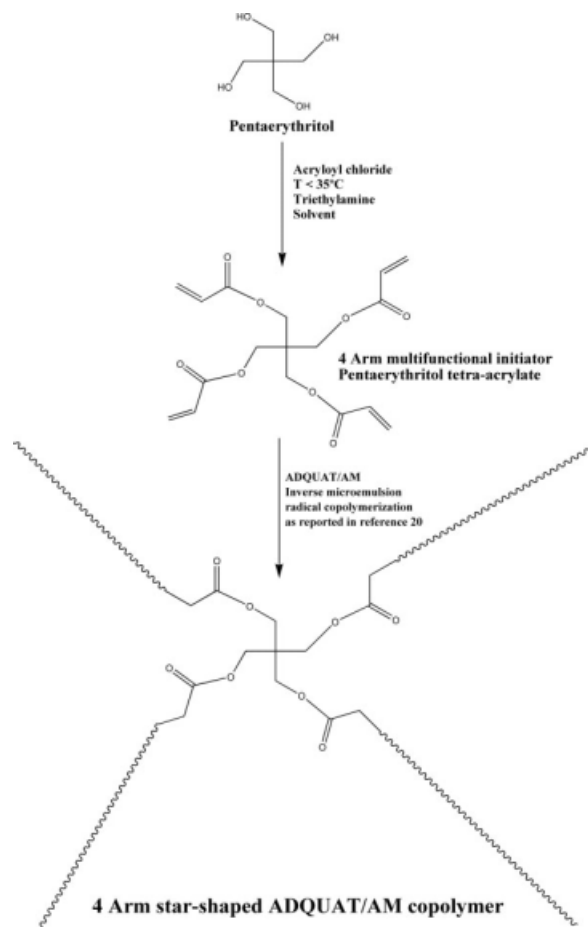
Structuring induced by isopropyl alcohol above a certain concentration can be explained because it can cause some sorbitan sesquioleate, one of the two isopropyl alcohol soluble surfactants used for obtaining the samples herein studied,<sup>20</sup> to be solubilized in the water phase of a microemulsion. Sorbitan sesquioleate is an interfacially radically active emulsifier with several labile (extractable hydrogens) hydroxyl functionalities on the hydrophilic head and a double bond on the hydrophobic moiety. Consequently, sorbitan sesquioleate can act as a terminating agent for the growing macromolecules through the extractable hydrogens on the hydrophilic head, producing an emulsifier radical. This transfer to the surfactant reaction lowers  $M_w$ , but the emulsifier radical polymerizes, generating a macroradical with a terminal double bond. These macroradicals contain terminal emulsifier groups with multiple reactive functional groups (extractable hydrogens of the hydroxyl groups and a double bond on the hydrophobic moiety), so they can participate in a chain-branching reaction cascade, which leads to high-molar-mass macromolecules.<sup>27</sup>

Therefore, from the standpoint of FP, between IPCs of 0 and 0.75 wt %, a net increase in FP is produced because even though both the slight increase in VSI and the strong decline in  $M_w$  should lead to a decline in FP, the shorter chains of the flocculants produced at the higher IPC are still long enough to improve FP by the particle bridging mechanism on account of their greater swelling capacities in aqueous solutions. The lower FP caused by the increase in VSI is counteracted by the higher FP due to the decline in  $M_w$ . This situation is also produced between IPCs of 0.75 and 1 wt %.

However, above this last value, VSI is practically constant, whereas  $M_w$  decreases dramatically by 75.1% with respect to the sample with no isopropyl alcohol added and by 61.9% with respect to the sample with the peak FP at an IPC of 1 wt %. The dramatic decline in  $M_w$  means that much shorter chains are obtained above an IPC of 1 wt %, and this prevents good flocculation action by particle bridging, resulting in a strong decrease in FP.

#### Proposed new family of star-shaped ADQUAT/AM flocculants

According to the results discussed in the previous sections, better FP is achieved by slightly structured ADQUAT/AM copolymers with  $M_w$ 's between 4 and  $5.9 \times 10^6$  g/mol. On the other hand, bridging



**Figure 10** Proposed synthetic pathway for obtaining four-arm, star-shaped ADQUAT/AM copolymers from pentaerythritol as a building block.

flocculation requires linear, high-molecular-mass flocculants that cannot be synthesized by inverse microemulsion polymerization at very high TCCs like the ones used herein. Consequently, if in a copolymer multiple linear chains of a suitable length could combine together under the same architecture, a remarkable increase in FP by the bridging mechanism could be expected. Such an architecture can be provided by star-shaped polymers in which multiple arms consisting of macromolecular chains extend from a central core.

A four-arm, star-shaped ADQUAT/AM copolymer is depicted at the bottom of Figure 10. If the molecular mass of every arm is between 1.5 and  $4 \times 10^6$  g/mol, on the one hand, a chain more linear than structured is to be expected according to the results herein obtained; on the other hand, superior FP is envisioned on account of enhanced bridging flocculation because the molecular mass of the star copolymer would range from 6 to  $16 \times 10^6$  g/mol. Larger and more robust flocs are expected. Star polymers have been shown to play an important role in inducing highly effective bridging flocculation.<sup>30,31</sup>

Likewise, in Figure 10(a), a possible synthetic route for obtaining four-arm, star-shaped ADQUAT/AM copolymers is depicted. Starting from pentaerythritol as a building block, the four-arm, multi-functional initiator pentaerythritol tetra-acrylate (PTA) can be synthesized by a reaction with acryloyl chloride in a suitable organic solvent at temperatures below 35°C in the presence of tetraethyl amine as an HCl scavenger. Then, PTA can be used in a suitable PTA/ADQUAT/AM molar ratio for obtaining the proposed star-shaped ADQUAT/AM copolymers by inverse microemulsion copolymerization under the experimental conditions reported in ref. 20.

It is obvious that different polyhydroxylic chemicals other than pentaerythritol could be used as building blocks to generate star ADQUAT/AM copolymers with different arm numbers.

## CONCLUSIONS

Inverse microemulsion samples of highly concentrated flocculants based on 80 : 20 wt % ADQUAT/AM with a copolymer content as high as 42 wt % were used to study the correlation between the inverse microemulsion copolymerization variables and FP; the CST test was used to assess FP on anaerobically digested sludges from a municipal water treatment plant. The following conclusions were drawn.

First, FP decreases as TCC increases even though  $M_w$  increases dramatically with TCC and this should lead to higher FP according to the bridging flocculation mechanism. The results can be explained if we take into account the increasingly structured nature of the copolymers, as measured by VSI, with TCC leading to a decrease in their swelling capacities in aqueous solutions, which does not favor flocculation by the bridging mechanism, and also to a shielding of their positive charges, which does not favor flocculation by charge neutralization.

Second, FP is almost independent of EC as a result of two counteracting factors: (1) less structured copolymers with a higher swelling capacity in aqueous solutions are obtained as EC increases, and this favors flocculation by the bridging mechanism, and (2)  $M_w$  decreases with EC, and this leads to copolymers with lower FP by particle bridging and also by charge neutralization because of the lower capacity for particle surface coverage.

Third, as HLB increases from 9 to 9.9, FP increases strongly up to 9.5 and then decreases slightly. Up to an HLB of 9.5, the  $M_w$  and BV increments are much higher than the VSI increment, and this suggests that the linearity of copolymer chains is only slightly reduced. As a result, cationic flocculants with longer chains and greater swelling capacities are obtained, with both features favoring flocculation by the bridging mechanism. Above an HLB of 9.5, FP

decreases slightly because  $M_w$  hardly varies with HLB but VSI increases also slightly, and this indicates that more branched copolymers are obtained.

Fourth, there is a relationship between FP and VSI and  $M_w$ . FP decreases with both, and this means that the best FPs are obtained with less structured copolymers with not too long chains.

Fifth, inverse microemulsion copolymerization does not allow us to obtain good AM-based cationic flocculants at the high solid concentrations demanded by the market unless a structuring-control agent such as isopropyl alcohol is used. In the system herein studied, below 1 wt % (with respect to TCC), isopropyl alcohol reduces  $M_w$  but avoids an VSI increase in such a way that copolymers with a higher swelling capacity are obtained, leading to an increase in FP in comparison with those obtained in the absence of isopropyl alcohol. Above 1 wt %, isopropyl alcohol dramatically reduces  $M_w$ , resulting in copolymers with not enough long chains for good flocculation by the bridging mechanism, and FP decreases.

Sixth, an unexpected behavior of isopropyl alcohol as a structuring inductor has been found above 0.5 wt %. Up to this concentration, the isopropyl alcohol behavior is as expected: VSI decreases with IPC. Above an IPC of 0.5 wt %, an increase in VSI is observed. This result is explained by the fact that isopropyl alcohol at the aforementioned concentration can solubilize in the water phase of a microemulsion some amount of one of the two surfactants used for obtaining the inverse microemulsion samples herein studied: sorbitan sesquioleate. Sorbitan sesquioleate is an interfacially radically active emulsifier that leads to more structured high-molar-mass macromolecules.<sup>27</sup>

Seventh, the experimental results allow us to envision that star-shaped ADQUAT/AM copolymers with molar masses ranging from 1.5 to  $4 \times 10^6$  g/mol per arm could be flocculants with superior FP. A synthetic route to four-arm, star-shaped ADQUAT/AM copolymers has been proposed.

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