Inhibition of calcium oxalate monohydrate by poly(acrylic acids) with different end-groups

W. O. S. Doherty*, C. M. Fellows, S. Gorjian, E. Senogles and W. H. Cheung

*Corresponding author, Chemistry Group, Sugar Research Institute, Mackay, Queensland 4740, Australia Fax +61 7 4952 7669 Phone +61 4952 7600 E-mail b.doherty@sri.org.au

SUMMARY

Water-soluble low molecular polymers are known to affect the crystal habit of scale forming minerals and their rates of deposition. Poly(acrylic acid) (PAA) and poly(maleic acid) are commonly used to control scale formation in sugar mill evaporators. Calcium oxalate (both mono- and dihydrate) forms the bulk of the hard intractable scale found in Australian sugar mills, causing efficiency losses of significant economic importance. In this work, the formation of calcium oxalate monohydrate in a synthetic juice solution was investigated in the presence of PAAs of varying molecular weight and end-group functionality and a strong dependence on both of these factors was observed. Terminal functionality was controlled using three chain-transfer agents (CTA); thioethanol, thioglycolic acid and dodecanthiol. Effectiveness of inhibition varied with CTA in the order thioethanol ~ thioglycolic acid > dodecanthiol for all molecular weights. This suggests that polymer end-groups play a role in scale inhibition. The polymers which were prepared with dodecanthiol accelerated rather than inhibited calcium oxalate formation, implying a different mode of action on calcium oxalate crystallization. Consistent with previous reports for other scales, the calcium oxalate inhibition tests show optimum effectiveness for PAAs of molecular weight 2000-4000.

Deleted: In the sugar milling industry, deposition of evaporator scales is of significant economic importance. These scales impair heat transfer and consequently reduce the thermal efficiency of the evaporator station. Calcium oxalate (both mono- and dihydrate) forms the bulk of the hard intractable scale found in Australian sugar mills.¶

Deleted: Australian

Deleted: Results of calcium oxalate inhibition tests show optimum effectiveness for PAAs of molecular weight 2000-4000.

Keywords: Acrylic acid, polyacrylic acid, precipitation polymerization, scale inhibitors, molecular weight determination

Introduction

Formation of scale on equipment surfaces is a problem in many areas such as industrial water systems, secondary oil recovery utilizing water flooding techniques, desalination and sugar mill evaporators. In the sugar milling industry, the deposition on evaporator units of mineral salts such as calcium oxalate (monohydrate and dihydrate), calcium magnesium aconitate, amorphous silica, calcium sulphate dihydrate, calcium carbonate and calcium phosphate is of major economic importance [1, 2]. Water-soluble low molecular weight polymers are often used as scale inhibitors in such systems. The effect of these species on the crystal habit of scale-forming minerals and on their rates of precipitation has been the subject of numerous investigations [3]. Senogles and Doherty [1] have investigated the use of low molecular weight polymeric additives such as poly(acrylic acid) (PAA) and poly(maleic acid) to control scale formation in Australian sugar mills. They demonstrated changes in calcium oxalate nucleation and crystal growth processes due to the adsorption of polymers on the surfaces of calcium oxalate crystallites.

In this work the formation of calcium oxalate in a synthetic sugar juice solution was investigated in the presence of PAA species of varying molecular weights while the same temperature, solution pH, and polymer concentration were maintained. Another variable that may determine the effectiveness of an inhibitor is the identity of the terminal functional group of the PAA chain. Three chain transfer agents (CTA) were therefore selected to control both molecular weight and end-group functionality of PAA. These were: thioethanol, which introduces a –OH group on the chain terminus, thioglycolic acid, which introduces a –COOH group, and dodecanthiol, which introduces a $–C_{12}H_{25}$ group. The CTAs were selected

Deleted:

Deleted: Among the problems caused by scale deposits are obstruction of juice flow, impedance of heat transfer and wear of equipment parts. Also, localized corrosion of the evaporator units can occur due to the harsh cleaning regimens used for scale removal

Deleted: If the evaporator units are the rate-limiting step in the factory, the sugar mill must stop production for cleaning purposes. Scale formation is enhanced at high sucrose concentrations because of reduced solubilities of calcium oxalate and silica. Composite fouling of calcium oxalate and silica occur in the fourth and fifth effects (evaporator units) of sugar mill evaporators where the temperatures of the units are lowest. As the working temperatures of these units are low, cleaning chemicals are not at their optimum resulting in reduced performance.¶
The effect of

Deleted: w

Deleted: maintaining

Deleted: chemical

Deleted: polymer

Deleted: As such t

for their effect on the ability of PAA to bind to calcium oxalate crystallites, on the basis of their relative affinity for ionic substrates. It was anticipated that the –COOH-terminated polymers would be most successful in binding to forming calcium oxalate surfaces, while the –OH-terminated polymers would be somewhat less effective and the $–C_{12}H_{25}$-terminated polymers least effective.

Experimental

Acrylic acid can be polymerized in bulk [5] or in aqueous or organic media by methods such as inverse-suspension [6, 7] or inverse-emulsion [8] polymerization. The rate of polymerization is dependent on the nature of the polar solvent, the ionic strength and the pH (for reactions carried out in aqueous solution) [9]. The maximum rate of polymerization occurs near the pK_a of acrylic acid, suggesting that the cross-propagation reaction between the acid and salt forms of acrylic acid may be favoured. The use of a precipitation polymerization method has been reported [10] to overcome the strong solvent dependence of the polymerization rates and eliminate contamination of polymer by emulsifying agents. The method uses an aromatic hydrocarbon such as toluene which is a solvent for the monomer and a non-solvent for the polymer. As the purity of the polymer will influence scale inhibition tests, precipitation polymerization was used in this study.

Synthesis

Glacial acrylic acid (Sumika Co., Singapore) was supplied inhibited with 200 ppm of hydroquinone monomethylether, and was degassed, but not otherwise purified, prior to polymerization. Toluene (BDH) and hexane (Certified ACS, BDH) were used without further purification. Azo-*bis*-isobutyronitrile (AIBN, Aldrich) initiator was recrystallized from methanol and light petroleum ether. The chain transfer agents 2-thioethanol and

dodecanthiol (Aldrich) were used without further purification and thioglycolic acid (Aldrich) was purified by distillation.

Acrylic acid (10g, 0.14 mol), toluene (90 mL) and a known amount of CTA were added to a three-neck-flask. A number of different CTA at various concentrations were used to give a rnage of molecular weights and end-group functionalities (Table 1). The reaction mixture was sparged continuously with nitrogen for 1 to 2 h at room temperature to remove any residual oxygen, and a known amount of AIBN was added under nitrogen as a solution in 5 mL N,N-dimethyl formamide. The reaction mixture was stirred at 50°C for 2 to 24 h under nitrogen. The precipitated polymers were filtered off, washed with n-hexane and dried to constant weight under air at 60°C for ~12 h.

Deleted: (see Table 1)

Polymer Characterization

Gel Permeation Chromatography

The synthesized PAAs were characterized by aqueous-phase Gel Permeation Chromatography (GPC) to estimate the number average molecular weight, M_n. GPC analysis was carried out using a Waters Gel Permeation Chromatograph (Model 441) with an Erma dRI Model ERC 750 detector. M_n was determined using (a) 0.5 M $LiNO_3$ and (b) 0.5 M NaCl buffered to pH 9 as eluent. For method (a), *Mn* was estimated using polyethylene oxide (PEO) standards (4 standards covering the molecular weight range from 29600 to 761300, Mark-Houwink parameters $K = 3.47 \times 10^{-4}$, $a = 0.700$ [11]). For method (b), these same PEO

Deleted:

Deleted: determine

Formatted: Font: Italic

standards were used and a calibration done using Mark-Houwink parameters for poly(sodium acrylate) under the given conditions, $K = 2.44 \times 10^{-5}$, $a = 0.887$ [12]. As there were differences in the M_n values determined by the two approaches, the M_n values given in Table 1 have been scaled from values obtained in separate runs with $LiNO_3$ to agree with the results for two samples that gave similar results with NaCl.

Figure 1 illustrates the dependence of M_n on the concentration and type of CTA for concentrations up to 0.02 $molL^{-1}$. As expected, lower molecular weight polymers are obtained at higher concentrations of CTA. However, a marked difference is seen between the effectiveness of the different chain transfer agents, as shown in Figure 1. At similar CTA concentrations, both thioethanol and TGA gave comparable M_n values while dodecanthiol gave higher values. Literature values of chain transfer coefficients for CTAs for thioethanol and alkyl thiols are very similar for acrylate and methacrylate polymers [11], making the large difference between the effectiveness of thioethanol and dodecanthiol surprising. A possible explanation for thioglycolic acid producing polymers of lower molecular weight than dodecanthiol is that as a more polar species it is preferentially concentrated near the growing polymer chains, rather than being distributed evenly throughout the toluene solution.

At low CTA concentrations, a trend to lower molecular weight at longer reaction times can be seen. This is to be expected giving normal termination mechanisms in a system such as the one employed where the initiator concentration remains relatively constant (the half-life for AIBN at 50°C in toluene is approximately 90 h [11]) while the monomer concentration is declining. At higher concentrations of CTA, this effect is masked by chain transfer to the thiol.

Nuclear Magnetic Resonance Spectroscopy

The synthesized PAAs were examined by proton magnetic resonance spectroscopy (^{1}H-NMR) to locate groups associated with the CTAs. Typical NMR spectra for PAA prepared with each of the CTA are presented in Figure 2. The broad signal at about 4.4 ppm is assigned to protons on the thioether methylenes attached to no other functional group, i.e., PAA-CH_2SCH_2- for thioethanol and dodecanthiol and PAA-CH_2S- for thioglycolic acid-terminated PAAs. The broadness of the signal is indicative of a covalent bond between CTA and the polymer chain and not due to unreacted CTA. The number-average molecular weight, M_n, was then estimated from the ratio of end-groups to the signals from the backbone methine and methylene resonances, assuming an incorporation of one CTA molecule per polymer molecule. In general, the NMR method for M_n determination gave results similar to those obtained in Table 1 (± 20 %).

Deleted: a

Calcium oxalate monohydrate inhibition test

Calcium oxalate inhibition was tested using a solution with sucrose and organic and inorganic ion concentrations equivalent to those found in cane sugar juice. Table 2 shows the composition of the synthetic juice used in this study. The juice was adjusted to pH 7.0 with sodium hydroxide, filtered through a 0.45 μm membrane and used within 24 h of preparation.

The evaluation of polymers for calcium oxalate monohydrate inhibition involved adding 200 mL of synthetic juice to a very clean 250 mL beaker with no cracks or surface imperfections. Exactly 40 ppm of oxalic acid was added to the juice followed by 3 ppm polymer. The mixture was boiled, with stirring, at atmospheric pressure until visible turbidity indicated calcium oxalate monohydrate precipitation. The beaker was then removed from heat, covered, and cooled to room temperature, upon which sucrose concentration was determined by measurement of the refractive index of the solution. The effectiveness of the polymer for the desired application is best determined by the extent to which it retards the onset of

turbidity in comparison to a solution to which no polymer was added. This is expressed in terms of percent inhibition (*I*), defined as

$$I = \frac{S\% - 17\%}{46\%} \quad (1)$$

where *S*% is the percentage of sucrose in the final turbid solution and 17% is the percentage of sucrose in juice concentrated without the use of a scale inhibitor. The term 46% is the difference between *S*% and 63%, the target concentration of sucrose in the product emerging from the final evaporator stage in the factory.

Scanning Electron Microscopy

The crystal sizes and shapes of calcium oxalate formed in the presence and absence of polymers were examined in a JEOL 5410LV scanning electron microscope operating an accelerating voltage of 10 kV.

Results for calcium oxalate monohydrate inhibition

The *I* values obtained for the PAAs are given in Table 3, together with figures for the commercial PAA scale inhibitors Antiprex A and Evaptreet XY. Selected values are displayed graphically in Figure 3, showing *I* as a function of M_n for each series of PAAs investigated. Each data point is an average of a number of experiments with an error of ± 2%.

The effectiveness of the polymers in preventing calcium oxalate formation improves at lower PAA molecular weight. For PAAs prepared with thioethanol and thioglycolic acid, optimal scale inhibition occurs at M_n between 2000 and 4000. Dodecanthiol-terminated PAAs, however, give relatively poor scale inhibition whatever their molecular weight.

Crystal morphologies of calcium oxalate monohydrate

Scanning Electron Microscopy (SEM) was carried out on the calcium oxalate monohydrate samples obtained from the inhibition tests. A number of representative SEM images are shown Figures 4, 5 and 6. Figure 4 is the micrograph for calcium oxalate monohydrate prepared in the absence of polymer. The crystals are not well developed, with an irregular laminar appearance. When calcium oxalate monohydrate is prepared in the presence of PAA with –COOH end groups (i.e., with thioglycolic acid), an effective scale inhibitor, some of the crystals are cruciform but a large majority of the crystals have poorly developed faces, approaching spherical symmetry (Figure 5). However, when calcium oxalate monohydrate is prepared in the presence of PAA with $-C_{12}H_{25}$ end-group (i.e. with dodecanthiol), a poor scale inhibitor, uniformly produced plate-like structures are formed (Figure 6). The small crystal sizes formed suggests that 'shock' crystallization has taken place.

Discussion

The best PAA scale inhibitors prepared show equivalent effectiveness to commercial antiscalants (Table 3). It is suggested that the PAA acts to inhibit scale formation by adsorption to the surface of growing calcium oxalate crystallites, preventing crystallite growth. The observed optimum in inhibition efficiency as a function of molecular weight (Figure 3) may be explained with reference to two conflicting size-related trends. As PAA increases in size, its adsorption will become less reversible due to the increasing number of carboxylic acid groups per polymer that can interact with the surface. Above an optimum molecular weight, however, the polymer chain will not be able to relax completely on the crystallite surface within the timescale of interparticle interactions and monolayer growth [1].

Deleted: scale inhibitors

This will reduce the proportion of acid groups able to interact directly with the crystallites, and this extended polymer may also behave as a coagulant/flocculant, aggregating and bridging crystallites to give qualitatively less effective inhibition. This result is consistent with previous reports for a number of scales and antiscalants [13, 14]. It is also probable that at an optimum molecular weight, the polymer is able to completely wrap around the crystallites and cause repulsion between them, enhancing inhibition.

Thioglycolic acid (i.e., –COOH) and thioethanol (-OH) derived end-groups are expected have a much higher degree of adsorption than dodecanthiol because they are capable of polar interactions with the crystallites, and can be seen to be effective in reducing the rate of crystal growth from their effect on morphology (Figure 5). The $C_{12}H_{25}$ end-group will not adsorb to the calcium oxalate surface, and because of its size could provide a reservoir of thermal energy for desorption of the polymer from the crystallite surface. Furthermore, the hydrophobic character given to PAA by the $C_{12}H_{25}$ end-group could result in the formation of an insoluble complex with calcium. The calcium-polymer complex micro-particles would then act as seeds for 'shock' crystallization of calcium oxalate (Figure 6). Even at a low polymer molecular weight where the polymer backbone chain is short, the dangling hydrophobic chain ends of $–C_{12}H_{25}$ may foster aggregation of the calcium oxalate crystallites and therefore cause rapid calcium oxalate precipitation.

The enhanced growth of calcium oxalate observed under some conditions in this work when $C_{12}H_{25}$-terminated polymers were employed suggests that the use of such an additive in a sugar factory would result in the formation of calcium oxalate at an earlier stage in the multistage juice evaporation process. Calcium phosphate, the major component of scale in the earlier evaporator units, is regarded as 'soft scale' since it readily removed by acid, and earlier formation of calcium oxalate scale will give a composition of mixed calcium

Deleted: will

Deleted: bind in this way

Deleted: coagulation/flocculation

Deleted: f

Deleted: before the final effects

Deleted: effects

Deleted: . Early

Deleted: with

phosphate and calcium oxalate in the early effects. Once the calcium phosphate is dissolved the calcium oxalate component of the scale will be easily dislodged and removed.

Deleted: This mixture will be easier to remove than calcium oxalate because on

Deleted: An added advantage in causing calcium oxalate to form in earlier effects is that during chemical cleaning, these vessels can be operated at far higher temperatures than the later effects, which will facilitate the solubilization of scale .

Conclusions

Inhibition tests of calcium oxalate monohydrate formation using PAAs of varying molecular weight gave marked differences in inhibition behaviour were observed for different chain transfer agents independent of the molecular weight determined, with effectiveness declining with end-group type in the order thioethanol ~ thioglycolic acid > dodecanthiol. This suggests that polymer end-groups play a role in the adsorption of polyacrylic acid to the growing calcium oxalate crystallite surface. The PAAs with end-groups that are capable of adsorption on to the crystallite surface were significantly more effective than those with end-groups less likely to adhere to the crystallite surface.

Deleted: suggest that optimum effectiveness for PAAs is given by a molecular weight in the range 2000 to 4000. D

Deleted: most

Deleted: that cause weak adsorption

Acknowledgements

We gratefully acknowledge the assistance of Mrs Jelica Strauch of the Key Centre for Polymer Colloids at the University of Sydney and Ms Kaye Falzon of the Sugar Research Institute for contributions to the project. The financial support of the Sugar Research and Development Corporation (SRDC) is gratefully acknowledged.

References

1. E. Senogles, W.O.S. Doherty and O.L. Crees, *Scale Inhibitors, Polymeric*, in *Encyclopedia of Polymer Science and Technology*, J. Kroschwitz, Ed. Wiley-Interscience: New York. 7587 (1996).
2. P. Honig, in *Principles of Sugar Technology*, P. Honig, Editor. Elsevier: Amsterdam (1996).
3. E. R. McCartney and A.E. Alexander, *J. Colloid. Sci*., **13**, 383 (1996).
4. Z. Amjad, J.F. Zibrida and J.A. Thomas-Wohlever, *Inhibition of calcium phosphate precipitation by polymers in the presence of iron(III): The influence of chelating agents.* Book of Abstracts, 218th ACS National Meeting, New Orleans, Aug. 22-26, 1999.
5. A. Chapiro and T. Sommerlatte, *Eur. Polym. J.*, **5**, 707 (1969).
6. S. Harada and H. Yamasaki. U. S. Patent 4446261 (1984).
7. F. W. Stanley, J.C. Lamphere and Y. Chonde. U. S. Patent 4833198 (1989).
8. K. Plochocka and J.C. Chuang. U. S. Patent 5216070 (1993).
9. F. D. Kuchta, A.M. van Herk and A.L. German, *Macromolecules*, **33**, 3641 (2000).
10. C. Bunyakan and D. Hunkeler,. *Polymer*, **40**, 6213 (1999).
11. J. Brandrup, E.H. Immergut and E.A. Grulke, Eds. *Polymer Handbook*. 4th ed., John Wiley & Sons: New York (1999).
12. K. J. McCarthy, K.J., C.W. Burkhardt and D.P. Parazak, *J. App. Polym. Sci.*, **33**, 1683 (1987).
13. Z. Amjad, *Desalination*, **54**, 263 (1985).
14. M. Okamoto, *Nippon Kagaku Kaishi*, **9**, 1153 (1986).

Figure 1. Dependence of molecular weight on the concentration of chain transfer agents. No CTA, ○; thioglycolic acid, '; thioethanol, !; dodecanthiol, %.

Figure 2: ^{1}H-NMR spectra of poly(acrylic acid) with (a) thioethanol end-groups (b) thioglycolic acid end-groups and (c) dodecanthiol end-groups. Signals wholly or partly derived from low-molecular weight impurities are marked with an asterisk.

Figure 3. Relationship between molecular weight and calcium oxalate monohydrate inhibition: No CTA, ○; thioglycolic acid, '; thioethanol, !; dodecanthiol, %. Antiprex A, + and Evaptreet XY, ×.

Figure 4. Calcium oxalate monohydrate (width of micrograph = 26.4 μm) in the absence of an additive.

Figure 5. Calcium oxalate monohydrate prepared in the presence of PAA with thioglycolic acid (width of micrograph = 26.4 μm).

Figure 6. Calcium oxalate monohydrate prepared in the presence of PAA with dodecanthiol (width of micrograph = 26.4 μm).

Table 1. Poly(acrylic acids) prepared with different chain transfer agents (CTA)

Type of CTA	CTA concentration ($molL^{-1}$)	AIBN concentration ($molL^{-1}$)	Reaction Time (h)	Molecular weight (M_n)
None	0	0.0024	24	12,800
Thioglycolic acid	0.0010	0.0012	24	9300
	0.0020	0.0018	24	5900
	0.0025	0.0024	2	5900
	0.0050	0.0024	24	4200
	0.010	0.0024	24	3300
	0.018	0.0024	2	3100
	0.040	0.0024	24	1600
	0.100	0.0024	2	1300
Thioethanol	0.0018	0.0018	3	4500
	0.0018	0.0018	6	3900
	0.0018	0.0018	16	4000
	0.0025	0.0024	2	5600
	0.0064	0.0024	2	3500
	0.0120	0.0024	2	3000
Dodecanthiol	0.0025	0.0024	2	14,500
	0.0025	0.0024	18	7800
	0.0050	0.0024	2	15,900
	0.0050	0.0024	24	11,800
	0.010	0.0024	24	5600
	0.010	0.0024	2	5700
	0.100	0.0024	24	2900
	0.100	0.0024	2	2800

Table 2. Synthetic juice formulation

Compound	**Juice ($molL^{-1}$)**
Sucrose	0.3768
Calcium chloride dihydrate	0.0061
Magnesium sulphate heptahydrate	0.0037
Potassium chloride	0.0210
Sodium gluconate	0.0018
Citric acid	0.0005
Aconitic acid	0.0110

Table 3. Effect of poly(acrylic acid) species on calcium oxalate inhibition

Type of CTA	**Molecular weight (M_n)**	**Percentage Inhibition *(I)***
None	12,800	13
Thioglycolic acid	9300	-2
	5900	39
	5900	7
	4200	28
	3300	63
	3100	54
	1600	37
	1300	7
Thioethanol	4500	43
	3900	78
	4000	43
	5600	13
	3500	50
	3000	91
Dodecanthiol	14,500	-7
	7800	-4
	15,900	-7
	11,800	9
	5600	-7
	5700	2
	2900	11
	2800	15
Antiprex A		89
Evaptreet XY		91