



Apparent inhibition of thermal decomposition of hydrogencarbonate ion by poly(acrylic acid). The effect of molar mass and end-group functionality

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HIGHLIGHTS

- Alkaline scale formation is a thermodynamically controlled process.
- Polyacrylic acid appears to prevent heterogeneous decomposition of hydrogencarbonate.
- Hydrophobic end-group functionalization improves this behavior by 8 to 12% (at 10 ppm).

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ABSTRACT

The thermal decomposition of the hydrogencarbonate ion has been previously described by a bimolecular mechanism or a unimolecular mechanism. In this work the Gibbs free energy of the competing reactions for both the unimolecular and bimolecular mechanisms was calculated for typical concentrations found in thermal desalination plants. Activity coefficients were estimated using the Pitzer equations. At low temperature the bimolecular mechanism is thermodynamically favored, while above 80 °C the unimolecular mechanism is favored, consistent with observations of alkaline scale formation in thermal desalination plants. The rate coefficient of thermal decomposition of HCO_3^- at 97.2 °C in the absence and presence of 10 ppm of poly(acrylic acid) (PAA) with different end groups and molar mass was determined. PAA was found to retard the rate of decomposition by up to 49% and for all end groups of PAA the rate coefficient of thermal decomposition of 40 ppm HCO_3^- increased with increasing molar mass. The results are consistent with PAA preventing heterogeneous decomposition of HCO_3^- on interfaces. The rate of partitioning of PAA to these interfaces should increase with decreasing molar mass and resulting mobility of PAA, and may also be affected by self-assembly behavior.

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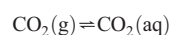
1. Introduction

Alkaline scale, composed primarily of calcium carbonate and magnesium hydroxide, is one of the main operational problems in the thermal desalination of seawater [1]. Historically the main method used in multi-stage flash (MSF) desalination plants to control scale formation has been acid treatment. This involves addition of acid, most often sulfuric acid due to its low cost, to maintain the pH of seawater at around 4.5 [2]. It is clearly desirable to reduce the amount of mineral acid used in thermal desalination. A means of scale control that has gained in importance in recent decades is the use of scale inhibitors, chemical additives that can control scale formation and/or deposition at ppm concentrations. These are either low molar mass organic compounds, typically phosphonates, or polymers of

approximate molar mass 1000–4000, typically containing carboxylate, sulfonate or phosphonate groups [3]. The efficiency of scale inhibitors depends on the system to which they are applied (ion concentration, temperature pH, and pressure) as well as on their chemical properties (functionality, molar mass, polydispersity, and structure) and usage (concentration and method of application). While a dosing rate of scale inhibitors below optimum leads to scale formation, overdosing can enhance sludge formation, and the level of addition has been progressively reduced over the past decades, to as little as <1 ppm [4].

1.1. The chemistry of alkaline scale

The formation of alkaline scale from seawater depends on the carbonic acid species equilibria, which in turn depend on the pH, temperature, and ionic strength of seawater [5].



Re.1

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Two main mechanisms have been proposed to explain the formation of alkaline scale in thermal desalination plants: the bimolecular mechanism proposed by Langelier et al. in 1950 [6] and the unimolecular mechanism proposed by Dooly and Glater in 1972 [7]. In both mechanisms, the first step is the thermal decomposition of hydrogencarbonate ion HCO_3^- (Re. 5).



Although the thermal decomposition of HCO_3^- is a bimolecular reaction as written above, it was reported to follow first order kinetics by Dooly and Glater [7]. This can be rationalized by postulating two primary first-order steps. The first of these steps is:



Where the hydroxide ion may also be generated by the reaction:



In the absence of any competing reaction, the second primary step is then a fast acid–base neutralization



The ultimate scale forming reactions in this system are the reaction of the anions generated with alkaline earth cations.



It is currently believed that both bimolecular and unimolecular mechanisms can occur under desalination conditions [2,8,9]. The mechanism of alkaline scale formation is likely to be a complex process involving competitive equilibria between unimolecular and bimolecular reactions. Many parameters such as supersaturation, temperature, mixing conditions, impurities, homogenous and heterogeneous nucleation and the effect of additives effective on calcium carbonate and magnesium hydroxide formation need to be considered and it is difficult to separate and investigate these parameters independently [10].

1.2. The effect of scale inhibitor on the thermal decomposition of HCO_3^-

As for all kinetically controlled reactions, the thermal decomposition of HCO_3^- can be catalyzed and inhibited by specific agents. To our knowledge, only three studies have been published on the effect of scale inhibitor on the thermal decomposition of HCO_3^- , all of which used commercial scale inhibitors [2,8,9].

1.2.1. Walinsky and Morton [8]

The effect of a commercial scale inhibitor (Flocon Antiscalant 247, 10 ppm poly(maleic acid)) on the kinetics of thermal decomposition of HCO_3^- and hydrolysis of CO_3^{2-} in refluxing synthetic brine containing ^{14}C -radiolabelled sodium hydrogencarbonate (375 ppm), calcium (824 ppm) and magnesium (1260 ppm) was investigated by Walinsky and Morton. The rate of decomposition of HCO_3^- in the absence and presence of scale inhibitor was monitored by radiochemical liquid scintillation assays of evolved $^{14}\text{CO}_2$. The results showed a decrease in the rate of decomposition of HCO_3^- in the presence of scale inhibitor,

with the overall first order rate coefficient declining from 0.20 min^{-1} to 0.05 min^{-1} . An increase in the rate of decomposition was seen in the presence of calcium and/or magnesium. They suggested the retardation of decomposition of HCO_3^- in the presence of scale inhibitor proceeded either via sequestration of Ca^{2+} and/or Mg^{2+} , inhibiting the calcium and magnesium catalyzed decomposition of HCO_3^- , or by preventing the heterogeneous decomposition of HCO_3^- on scale surfaces.

1.2.2. Mubarak [9]

Refluxing of seawater with and without commercial scale inhibitor (Belgard 2000, 10 ppm (poly(maleic acid))) for 5.5 h under either partial vacuum ($6.9 \times 10^4 \text{ Pa}$) or purging nitrogen was carried out by Mubarak. The decomposition of HCO_3^- could be described by a first-order mechanism with a rate constant of $9.7 \times 10^{-4} \text{ min}^{-1}$ for the unimolecular decomposition of the hydrogencarbonate ion (Re. 6) and $6.6 \times 10^3 \text{ min}^{-1}$ for the acid/base neutralization between hydroxide and hydrogencarbonate (Re. 8) in the absence of inhibitor. In the presence of 10 ppm of Belgard 2000, the rate of Re. 8 was unaffected while the rate coefficient of Re. 6 decreased to $9.4 \times 10^{-4} \text{ min}^{-1}$. Mubarak demonstrated that both HCO_3^- and generated OH^- were available in the same time in solution during the decomposition of HCO_3^- at 90°C . The hydrolysis of CO_3^{2-} as Na_2CO_3 for 1 h at 100°C showed no significant release of hydroxide ion or loss of CO_3^{2-} , results compatible with the Dooly and Glater Mechanism. Mubarak did not suggest a mechanism for the inhibition of thermal decomposition of HCO_3^- by scale inhibitor.

1.2.3. Shams El-Din et al. [2]

The most comprehensive study to date on the effect of scale inhibitor on the thermal decomposition of HCO_3^- was by Shams El-Din et al. The effect of three different polymaleate commercial scale inhibitors on the thermal decomposition of HCO_3^- (150 ppm) was studied in 4% NaCl solution at 100°C . The results were consistent with the Langelier mechanism with the concentrations of HCO_3^- , CO_3^{2-} and OH^- changing throughout the experiment as 2HCO_3^- converted to CO_3^{2-} and then to 2OH^- . According to the kinetic model used by Shams El-Din et al. for decomposition of HCO_3^- , hydrolysis of CO_3^{2-} only began after $[\text{HCO}_3^-]$ dropped to zero. The effect of scale inhibitor on the thermal decomposition of HCO_3^- was clearly on the rate constant of thermal decomposition of HCO_3^- which decreased with increasing of scale inhibitor concentration for all three different scale inhibitors, however by different values. Those results were obtained in the absence of calcium or magnesium ions, suggesting that one obvious explanation for the effect of polymeric scale inhibitor advanced by Walinsky and Morton, complexation of divalent ions by the PAA so they cannot catalyze hydrogencarbonate decomposition, cannot be correct. Shams El-Din reported that the different behavior for the scale inhibitors arose from differences in structure, molar mass and copolymer composition of the scale inhibitors but did not suggest a mechanism for their action.

1.2.4. Objective of this study

The objective of this work is to further investigate the role of polycarboxylic acids in controlling the decomposition of the hydrogencarbonate ion, using a series of well-characterized-PAA prepared by atom transfer radical polymerization (ATRP) in order to propose a mechanistic basis for any differences in effectiveness observed for different scale inhibitors. Conductivity measurements are applied to assess the capacity of PAA with different end-groups and controlled molar masses in retarding the thermal decomposition of HCO_3^- in boiling water ($97.2 \pm 0.5^\circ\text{C}$).¹ The important difference between this study and previous work is that the scale inhibitors which were used in this study have been synthesized using controlled radical

¹ Experiments were carried out in equilibrium with the atmosphere at an elevation of approximately 1000 m.

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