Synthesis, Characterisation and Application of Polymeric Scale Inhibitors

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Declaration

The work described in this thesis was carried out at the Department of Chemistry at the University of New England under the supervision of Dr. Christopher M. Fellows.

I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

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Abstract

Desalination of seawater by both the evaporation (e.g. multi stage flash, MSF) and membrane (e.g. reverse osmosis, RO) processes encounters difficulties with precipitation of sparingly soluble inorganic salts such as calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$) and calcium sulfate ($CaSO_4$). These precipitate during the desalination process when their solubility product K_{sp} is exceeded. To control this scaling problem, several methods for scale prevention and control are used, such as acid and additive treatments. Scale inhibitors are chemical additives that have gained importance in controlling scale formation and/or deposition in recent decades. These are low molecular weight organic compounds, typically phosphonates, or polymers of molecular weight 1000-4000, typically containing carboxylate, sulfonate or phosphonate groups.

In Chapter one, a brief summary of the mechanism of scale formation and scale inhibitors in desalination plants is given. The synthesis and characterisation of poly(acrylic acid) (PAA) with different end groups and molecular mass using Atom Transfer Radical Polymerization (ATRP) is explained in detail in Chapter two. In Chapter three the inhibition efficiency of PAA with different end groups and molecular mass to prevent the homogenous formation of calcium carbonate scale at low and elevated temperatures is studied. The best inhibition efficiency was found for low molecular mass of PAA with hydrophobic middle length end group (n-hexyl isobutryate, HIB) under most conditions.

Chapter four focuses on the effect of PAA with different end groups and molecular mass in the thermal decomposition of bicarbonate (HCO_3^-) at high temperature. Low molecular mass PAA with hydrophobic middle length end group (HIB) and long end group (decyl-isobutryate, DIB) was found to have the lowest rate coefficient for thermal decomposition of bicarbonate (HCO_3^-). In Chapter five a type of intrinsic exposed core optical fibre sensor (IECOFS) was used to study the heterogeneous crystallization of $CaCO_3$ and coprecipitation of $CaCO_3$ and $CaSO_4$ in the absence and presence of PAA at 100 and 120 °C. The attenuation of IECOFS and scanning electron microscope (SEM) results showed there was no heterogeneous crystallization of $CaCO_3$ on optical fibre surface in the presence of HIB-PAA (M_n = 1403 g/mol) and PAA (M_n = 1687 g/mol) with the longest hydrophobic end group (hexadecyl-isobutyrate, HDIB).

In Chapter six the homogeneous crystallization of $Mg(OH)_2$ in the absence and presence of low molecular mass ($M_n \leq$ 2000 g/mol) PAA with different end groups is discussed at 100 °C. The results showed a significant decrease in crystal growth of $Mg(OH)_2$ in the presence of PAA with different end groups. In Chapter seven, the inhibition efficiency of PAAs to prevent the homogeneous formation of calcium oxalate (CaC_2O_4) at low and high temperatures is studied. The highest inhibition efficiency of PAA with different end groups was at molecular masses between 1400 and 3300 g/mol. At low and high temperatures, a strong effect of the end-group was found. PAA with hydrophilic (CMM) and longer hydrophobic end groups (HDIB) have a performance better PAA with short (EIB) and middle (HIB &CIB) end groups. At 80 °C however, the effectiveness of the inhibitors terminated with middle hydrophobes was better than other end groups.

Abbreviations

ΔG	Gibbs free energy
$2\theta_{Mc}$	The interaction parameters of *M* with major cations (c) in solution
ATRP	Atom Transfer Radical Polymerization
B_{Ma} , C_{Ma}	The interaction parameters of *M* with major anions (a) in solution (ionic strength dependence)
c, a	cations and anions
CF	Concentration factor of brine solution
CIB	Cyclohexyl- isobutyrate
CMM	Carboxymethyl-1,1-dimethyl
COD	Calcium oxalate dihydrate
COM	Calcium oxalate monohydrate
COT	Calcium oxalate trihydrate
CGR	Crystal growth rate
DIB	Decyl- isobutyrate
EIB	Ethyl- isobutyrate
Eq-	Equation
FTIR	Fourier Transform Infrared spectroscopy

f^{γ}	The limiting Debye-Hückel (a function of ionic strength)
GPC	Gel permeation chromatography
HDIB	Hexadecyl- isobutyrate
HIB	Hexyl- isobutyrate
I	Ionic strength
IE	Inhibition efficiency
IECOFS	Intrinsic exposed core optical fibre sensor
ITD of HCO_3^-	The inhibition of thermal decomposition of HCO_3^-
K	Conductivity ($S.cm^{-1}$)
k	rate coefficient
K_{sp}	Solubility product
m_i	The molality of ion i (number of moles per kg water)
MSF	Multi Stage Flash
n	The order of reaction
NMR	Nuclear Magnetic resonance spectroscopy
PAA	Poly(acrylic acid)
PDI	Polydispersity index

P*t*BA	Poly(*tert*-butyl acrylate)
Re.	Reaction
RI	Refractive index
RO	Reverse Osmosis
S	Salinity
SEM	Scanning Electron Microscope
SL	Supersaturation level
TBT	Top brine temperature
TDS	Total dissolved solids
THF	Tetra-hydrofuran
TIR	Total internal reflection
XRD	X-ray diffraction
β°_{Ma}, β^{1}_{Ma}, β^{2}_{Ma} and C^{ϕ}_{Ma}	Pitzer parameters temperature dependence
γ_M	Activity coefficient of cation (*M*)
γ_X	Activity coefficient of anion (*X*)
Λ	The equivalent conductance
λ	Limiting Equivalent conductivity

Ψ_{Mca}	The interaction parameters of *M* with major cations (c) and anions (a) in solution

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