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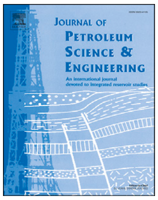

Hydrolysis kinetics of ATBS polymers at elevated temperature, via ^{13}C NMR spectroscopy, as basis for accelerated aging tests

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A R T I C L E I N F O

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A B S T R A C T

In offshore enhanced oil recovery application polymer residence time within the reservoir could be many years. Accelerated laboratory methods, for chemical stability testing, are therefore desired to perform efficient product type screening. For high temperature and/or salinity reservoirs co-polymers of acrylamide (AM) and acrylamide tertiary butyl sulfonic acid (ATBS) have become common in the industry. Simple high temperature storage was, however, not believed to be a viable accelerated test approach for these products. The reason being different hydrolysis rates for AM and ATBS, to acrylic acid (AA), as function of temperature. Hence the microstructure of a polymer aged at for example 120 °C should be significantly different from one stored at 80 °C.

To develop an accelerated testing methodology, improved understanding of hydrolysis kinetics is necessary. Aqueous solutions of AM-ATBS and AA-ATBS co-polymers were in the present work therefore stored at elevated temperature (70–140 °C) and progressive changes in microstructure followed by use of ^{13}C NMR spectroscopy. Short chained polymers (Mw ≈ 250 kg/mol) at high concentration (≈11%) were applied to reduce NMR scanning time.

In AM-ATBS co-polymers initial AM reaction rate followed a first order kinetic trend. After a significant hydrolysis (>20–30%) the kinetics of both AM and ATBS clearly deviated from first order and showed a distinct pH dependence. This was attributed to interaction with appearing AA neighbouring groups.

AA-ATBS co-polymers yielded higher hydrolysis rates than in AM-ATBS polymers, thus proving the intramolecular catalytic effect of AA on ATBS hydrolysis. A marked pH influence indicated the non-dissociated acid to be more efficient in catalysing ATBS removal than the carboxylate.

Polymer microstructure remained similar as function of hydrolysis degree in the whole studied temperature interval. This was herein proposed to stem from AM hydrolysis being the rate determining step. From a practical point of view this observation is intriguing as it indicates that simple high temperature storage could in fact be a viable route to accelerated laboratory screening of polymer stability.

A noticeable rate difference between pH 6 and pH 7 suggested that historically performed long term aging tests, in un-buffered solutions, may have yielded too optimistic predictions. Hence, a recommendation following the present work would be to critically evaluate whether to include pH buffering in future polymer stability tests.

1. Introduction

For offshore developments, well distances are generally long with fluid residence time that can range up to several years. Large distances, *i.e.* a limited number of wells, are often desired from a field development perspective. However, regarding polymer flooding for enhanced oil recovery (EOR) shorter distances may be a prerequisite due to the limited chemical stability at elevated temperature. Based on available data (Gaillard et al., 2015), (Swiecinski et al., 2016) (Seright et al., 2010), we crudely propose that for polyacrylamide (PAM) type polymers, long term stability is important for offshore fields with reservoir temperature exceeding 60 °C. Hence such cases require further investigation based on expected salinity, pH and exposure time.

During a laboratory qualification, one of the main criteria is the long-term stability of the chemical. Common practice is to test this aspect simply by storing polymer solutions anaerobically, in given brines, at the reservoir temperature. This 1:1 time in laboratory versus time in reservoir yields a very long lasting laboratory program obviously unsuited for

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investigating residence times of several years. In addition, efficient screening of various chemistries, or parameters impacting polymer stability, cannot be achieved. It is therefore desired to implement a workflow that can significantly accelerate the chemical stability evaluation. Alternatively, one could envision that with adequate data, for a given polymer type chemistry, laboratory verification of every product becomes superfluous.

1.1. *Thermal degradation*

It is well known that PAM type polymer solutions lose viscosity over time in hot (>60 °C) saline anaerobic environments. Generally, the loss of viscosity could be due to scission of polymer chains or by a change in polymer conformation. The former implies decreased chain lengths and the latter a more coiled up structure yielding a smaller hydrodynamic volume. During extended storage, the polymer side groups hydrolyse into acrylate/carboxylate (see Fig. 1) rendering the polymer more negatively charged. Subsequently the polymer chain becomes more susceptible to curl up, and eventually precipitate, when dissolved in hard brine. This mechanism is therefore commonly referred to as viscosity loss by hydrolysis.

In the absence of divalent ions (Seright et al., 2010) partially hydrolysed polyacrylamide (HPAM) polymers offer a very good stability and should for example maintain half of its viscosity for over 8 years at 100 °C. Thus, strongly suggesting that the loss of viscosity seen within months in high temperature laboratory tests must be due to hydrolysis rather than chain scission. Further support for this statement is for example given by (Gaillard et al., 2015) (Levitt and Pope, 2008), and (Ryles, 1988) that all showed viscosity loss to be pronounced in high divalent brines but virtually absent with low hardness. Hence except for low salinity/hardness water accelerated stability testing should regard hydrolysis as the prevailing mechanism.

HPAM polymers contain only two type of two side groups; acrylamide (AM) and acrylate (AA). Temperature and salinity tolerance of these PAM type polymers can be increased by adding other side groups like acrylamide tertiary butyl sulfonic acid (ATBS, see e.g. (Gaillard et al., 2015)) and/or N-Vinylpyrrolidone (NVP, see e.g. (Doe et al., 1987)). Although ATBS polymers are known (Moradi-Araghi et al., 1987) to be inferior to NVP polymers, regarding salinity and temperature tolerance, it is actually the former that in the later years seems to have become the preferred option up to around 100 °C. This is presumably due to higher molecular weights being available with ATBS than NVP *i.e.* lower costs associated with the reservoir polymer flood.

Herein we limit the investigation to ATBS type polymers. This is due to evaluation of target fields with a moderately high temperature (70–90 °C) where ATBS polymers are presently viewed as the most appropriate choice. The possible chemical groups are therefore acrylamide (AM), acrylamide tertiary butyl sulfonic acid (ATBS) and acrylic acid/acrylate (AA).

1.2. *Aim of study*

As mentioned above the aim is ultimately to construct a method for accelerated chemical stability testing of polymers in the laboratory. High temperature storage is commonly the approach for accelerating chemical reactions and would certainly also accelerate polymer hydrolysis. Time dependence could intuitively be found via an Arrhenius type of kinetic rate approach (Parker and Lezzi, 1993; Swiecinski et al., 2016). It is noted that this approach presupposes that there is only one chemical reaction or that several reactions possesses the same activation energy *i.e.* the same temperature dependence.

Regarding HPAM there is in principle only one chemical reaction (AM to hydrolyse into AA). However, there can be multiple factors affecting the rate of this single reaction, and in principle these may yield different temperature dependencies. The following rate influencing aspects have for example been discussed (Kheradmand et al., 1988):

1. Intramolecular catalysis by neighbouring un-dissociated carboxylate groups (Increases the rate at low pH *i.e.* Higher rate with increasing hydrolysis degree at low pH).
2. Catalysis by OH^- ions.
3. Electrostatic repulsion (Decreases the rate with increasing charge in the polymer chain *i.e.* Lower rate with increasing hydrolysis degree at high pH).

Therefore, AM conversion can be described as occurring along several mechanistic paths, implying that there is not truly only one chemical reaction yielding HPAM hydrolysis (Ryles, 1988) found that HPAM did

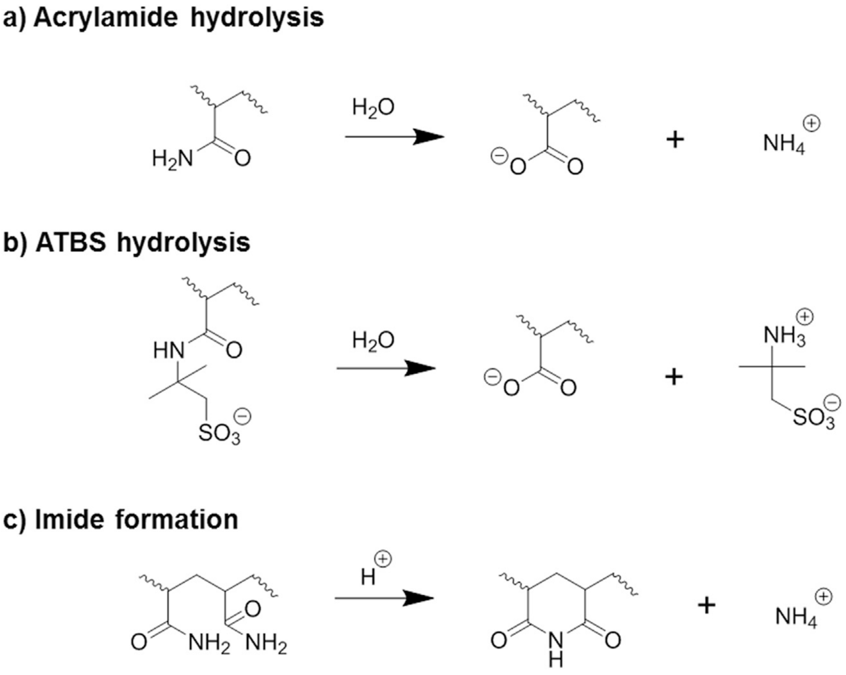

Fig. 1. Schematic of AM and ATBS conversion.