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Tris(tert-heptyl)-N-alkyl-1-ammonium bromides—Powerful THF hydrate crystal growth inhibitors and their synergism with poly-vinylcaprolactam kinetic gas hydrate inhibitor

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HIGHLIGHTS

- Quaternary ammonium salts with t-heptyl groups have been synthesized.
- These salts are outstanding THF hydrate crystal growth inhibitors.
- These salts are also excellent synergists for KHI polymers.
- Synergy is observed even when the quaternary salt is mostly oil-soluble.

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ABSTRACT

Quaternary ammonium salts containing the t-heptyl group have been synthesized for the first time. The new compounds are water-soluble tris(t-heptyl)(n-propyl)ammonium bromide and sparingly water-soluble tris(t-heptyl)(n-pentyl)ammonium bromide (tris(t-heptyl)PeAB). Both compounds were found to be powerful inhibitors of Structure II tetrahydrofuran hydrate crystal growth, with the performance of (tris(t-heptyl)PeAB) being as good as or better than that of either tetra(iso-alkyl)- or tetra(n-alkyl) ammonium bromides. Both t-heptyl salts were also excellent synergists in blends with poly(N-vinylcaprolactam) for kinetic hydrate inhibition of a Structure II-forming natural gas mixture using decane and 1.5 wt% aqueous NaCl at 80% water cut. This is all the more surprising for tris(t-heptyl)PeAB as this compound is sparingly water-soluble and thus partitions mostly to the liquid hydrocarbon phase.

1. Introduction

Some tetraalkyl quaternary ammonium and phosphonium salts are known to form clathrate hydrate structures (Jeffrey, 1984; Dyadin and Udachin, 1984). Examples are tetra(n-butyl)ammonium bromide (TBAB) and tetra(N-pentyl)ammonium bromide (TPAB). (Fig. 1) Since these salts have some common cluster features as Structure II (SII) gas hydrates they are able to act as crystal growth inhibitors of SII hydrates (Klomp et al., 1995; Klomp and Reijnhart, 1996; Klomp et al., 1997, Norland and Kelland, 2012). Studies on the crystal growth inhibition of tetrahydrofuran (THF) hydrate, which is a SII hydrate, have proven this. This property led to the use of TBAB and related salts as synergists in mixtures with kinetic hydrate inhibitor (KHI) polymers such as poly(N-vinylcaprolactam) (PVCap) to prevent gas hydrate formation in upstream oil and gas pipelines (Duncum et al., 1996a). Moreover, by lengthening one or two of the alkyl chains of the quaternary ammonium or phosphonium to about 12–16 carbon atoms to form cationic surfactants, it was found that these surfactants could control gas hydrate growth sufficiently to prevent hydrate agglomeration and allow dispersions of hydrate particles to form in a liquid hydrocarbon phase (Klomp et al., 1995; Klomp and Reijnhart, 1996, Klomp et al., 1997; Klomp, 1999; Klomp et al., 2004; Frostman and Downs, 2000; Frostman, 2000). Such cationic surfactants are known as gas hydrate anti-agglomerants (AAs) and have been used in oil and gas fields for over 15 years (Kelland, 2014).

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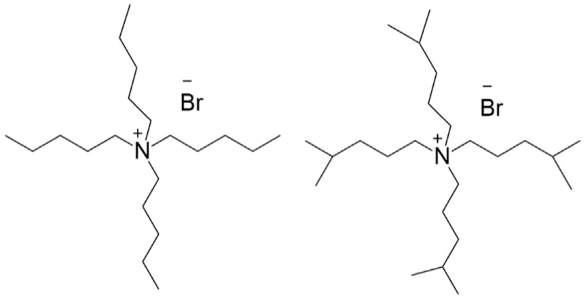

Fig. 1. Structures of tetra(n-pentyl)ammonium bromide and tetra(iso-hexyl) ammonium bromide.

Collectively, KHIs and AAs are known as low dosage hydrate inhibitors (LDHIs) as they are used at low concentrations (0.1–1 wt%) based on the water phase compared to the high concentrations (20–60 wt%) used for the more traditional thermo-dynamic inhibitors (THIs) such as methanol or monoethylene glycol (Kelland, 2006). Recently it was shown by our group that tetra(iso-hexylammonium) bromide (TiHexAB) was a superior inhibitor of THF hydrate crystal growth compared to the n-pentylated salt, TPAB (Chua and Kelland, 2012) (Fig. 1). The reason for this was presumed to be related to the optimal length of the n-alkyl/isoalkyl groups and the improved Van der Waals interaction with open SII hydrate cages with the isoalkyl branching at the end of the chains, compared to a straight alkyl chain. TiHexAB also gave significantly improved synergistic performance compared to TPAB or TBAB in kinetic hydrate inhibition tests when blended with PVCap.

The natural progression of these studies would be to investigate if there is improved hydrate crystal growth inhibition with t-hepylated (or 4,4-dimethylpentylated) ammonium salts where the end of the alkyl chain is now split into three methyl groups. It is known that a t-butyl group is small enough to fit inside the large $5^{12}6^4$ cavities of Structure II hydrate since it is known that neopentane (2,2-dimethylpropane) in mixtures with methane or dinitrogen forms a stable Structure II hydrate. The neopentane undoubtedly occupies the $5^{12}6^4$ cavities (Tohidi et al., 1997). We now report for the first time studies on the THF hydrate crystal growth inhibition and SII gas hydrate KHI synergy performance of t-heptylated ammonium salts with PVCap.

We assumed that tetra(t-heptyl)ammonium bromide (Tetra-tHepAB) would likely be insoluble in water at all temperatures since it was earlier found that tetra(n-heptyl)ammonium bromide (TetranHepAB) was water-insoluble. Therefore, we concentrated on reducing the hydrophobicity of one of the t-heptyl groups. We succeeded in synthesizing two salts containing the t-heptyl group, tris(t-heptyl)(n-propyl)ammonium bromide (tris(t-heptyl)PrAB) and tris(t-heptyl)(n-pentyl)ammonium bromide (tris(t-heptyl) PeAB) salts, both in reasonable yield. (tris(t-heptyl)PrAB) was found to be sparingly water-soluble. (tris(t-heptyl)PeAB) was found to be practically insoluble in water at 0–95 °C, which suggests that tetra(t-heptyl)ammonium bromide (which we did not attempt to make) is also likely to be sparingly soluble in water. However, (tris(t-heptyl)PeAB) was found to be soluble in THF/ water mixtures used in THF hydrate crystal growth inhibition experiments.

According to the above facts and in continuation our efforts to develop and investigate a new efficient classes of quaternary ammonium salt for oil and gas industry, we have designed and synthesized for the first time two quaternary ammonium salts attached with tertiary alkyl function group in the end of chain.

2. Experimental section

2.1. Materials and methods

All chemicals used in this work were purchased from Fluka, VWR or Sigma-Aldrich and were used without further purification. Melting points were determined on a Bibby Sterilin Ltd electro-thermal melting point apparatus and are uncorrected. All reactions were monitored by thin layer chromatography using Fluka GF254 silica gel plates with detection under UV light at 254 and 360 nm. NMR spectra were recorded on a Bruker Ascend NMR 400 MHz spectrometer at ambient temperature unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$) using TMS as internal standard. ^{13}C chemical shifts were related to that of the solvent. High resolution mass spectra (HRMS) were recorded on a ESI-MS Thermo LTQ Orbitrap XL (Infusion 5 μL/min, resolution: 100,000 at m/z 400, ca. 10 scans/ sample averaged). The molecular weight and molecular weight distribution of polymers was determined by gel permeation chromatography, using polystyrene samples as molecular-weight standards. Gel permeation chromatography was performed with a HLC 8220 chromatograph (Tosoh Co., Tokyo, Japan) equipped with TSK gel super HM-H H4000/H3000/H2000 (7.8 mm diameter, 150 mm × 3), Tosoh Co. Poly(N-vinylcaprolactam) (PVCap) was prepared according to our published procedure (Mady and Kelland, 2015).

2.2. General synthesis procedures

2.2.1. General procedure for cross-coupling of allyl bromide with tertiary alkyl Grignard reagent

A round-bottom flask was charged with allyl bromide (**1**) (120.9 mg, 1.0 mmol) and LiI (5.3 mg, 0.04 mmol) in a dry and nitrogen-flushed test tube equipped with a magnetic stirring bar. THF (10.0 ml) was added and the solution was cooled to −10 °C. *t*-BuMgCl (**2**) (0.81 M in 1.5 ml THF, 1.2 mmol) was added slowly followed by addition of isoprene (136.2 mg, 2.0 mmol) and anhydrous $CoCl_2$ (2.6 mg, 0.02 mmol). The cold bath was removed and the reaction mixture was warmed to room temperature, then heated at 50 °C for 5 h. The resulting mixture was cooled to 0 °C and the reaction quenched with 1M aqueous HCl (5 mL). The product was extracted with ether (3 × 20 mL), dried over $MgSO_4$, and concentrated under vacuum. The product was isolated by distillation from a round bottom flask (bp: 70.5–72.5 °C/760 torr) in 20% yield.

*4,4-dimethylpent-1-ene (**3**)* (Whitmore and Homeyer, 1933). liquid, ^1H NMR ($CDCl_3$, 400 MHz) δ 5.82–5.72 (m, 1H), 4.96–4.90 (m, 2H), 1.88 (d, J=8.0 Hz, 2H), 0.83 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.2, 116.4, 48.5, 30.7, 29.2.

2.2.2. Synthesis of 1-bromo-4,4-dimethylpentane (5)

In a dry 50 mL Erlenmeyer flask, a solution of 4,4-dimethyl-1-pentene (**3**) (3 g, 30.55 mmol, 1.0 equiv) and glacial acetic acid (10.0 mL) was stirring under nitrogen at −5 °C for 30 min. 30 wt% hydrogen bromide in AcOH (12.34 g, 1.5 equiv) was then slowly added dropwise to the reaction mixture under nitrogen. The mixture was stirring at −5 °C for 1 h and then overnight at room temperature. The mixture was carefully quenched with H_2O (20 mL) and subsequently extracted with ether (4 × 10 mL). The combined organic layers were washed with 1% potassium carbonate then brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, to obtain one product 1-bromo-4,4-dimethylpentane (**5**) with high selectivity and in good yield, 73%.

*1-Bromo-4,4-dimethylpentane (**5**)* (Whitmore and Homeyer, 1933). liquid, ^1H NMR ($CDCl_3$, 400 MHz) δ 3.32 (t, J=8.0 Hz, 2H),