



Universitetet
i Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

MASTER'S THESIS

Study programme/specialisation: Offshore environmental technology	Autumn semester, 2017 Open
Author: Samer Sahli (signature of author)
Programme coordinator: Supervisor(s): Malcolm A. Kelland	
Title of master's thesis: Investigation into method to raise the deposition point of kinetic hydrate inhibitor polymers	
Credits: 30	
Keywords: Kinetic hydrate inhibitor Cloud point Deposition point	Number of pages:37..... + supplemental material/other:0..... Stavanger,.....14/12-17..... date/year

Acknowledgments

This work was a long and demanding process that gave me great knowledge and understanding in this field. I would like to give my sincere thanks to my supervisor Malcolm A. Kelland for the support and guidance that was essential during this semester. Professor Kelland was always available for helping me during this tough time and he gave me encouragement to finish this paper. I give also thanks to Mohammad Mady for his guidance in the laboratory and for giving me great advice during this time.

I give my sincere thanks to my family for giving me all this support and understand. This would not be possible without the help and support from all member of my family.

Abstract

The use of kinetic hydrate inhibitor (KHI) to prevent gas hydrates from forming is a common practice in the oil and gas industry. KHIs are water soluble polymers that consists of a hydrophilic and hydrophobic parts giving them properties to delay hydrate nucleation and crystallization at low concentrations. Poly(N-vinylcaprolactam) (PVCap) and poly(N-isopropylmethacrylamide) (PNIPMAM) are examples of polymers that are used as KHIs. These polymers are water soluble at room temperature and have a cloud point (T_{cl}) at 30-40 °C and deposition point (T_{dp}) a few degrees above the T_{cl} . The use of additives such as salts, surfactants and denaturant agents can affect the T_{cl} and T_{dp} of a polymer. Another method to increase the T_{dp} of polymers is by copolymerization, but this method can have a negative effect on the performance of the KHI. Using additives to increase the T_{dp} of these polymers was studied in the laboratory and tests with different concentrations of polymers was carried to investigate the effect they had on PVCap and PNIPMAM. There was very rarely any significant effect on T_{cl} at concentration of 0.1-0.5 wt%, but some of the additives had significant effect on T_{dp} . The cationic polymers that had low M_w , such as PVAmine.HCl increased the T_{dp} of PVCap with increasing concentration. Possibly when the charge of the cationic polymer is close to the backbone of the polymer, the effect on the T_{dp} is much greater. The non-ionic additive trimethylamine oxide (TMAO) had impact on the T_{dp} of PNIPMAM. The anionic polymer sodium lignosulphonate was the only anionic additive that showed to increase the T_{dp} of PVCap. Performance tests of the KHIs showed that the sodium lignosulphonate had little effect on the performance on PVCap and TMAO had little negative effect on the KHI performance of PNIPMAM.

Table of Contents

Front page	1
Acknowledgments	2
Abstract	3
1. Introduction.....	5
1.1 Background.....	5
1.2 Gas Hydrate Structure	7
1.3 Kinetic hydrate inhibitors	8
1.3.1 Poly(N-vinylcaprolactam) (PVCap)	8
1.3.2 poly(N-isopropylmethacrylamide) (PNIPMAM)	9
1.4 Cloud point and deposition point.....	10
1.5 Methods to raise cloud point and deposition point.....	11
1.5.1 Salt and Hofmeister series	11
1.5.2 Denaturing agents	12
1.5.3 Copolymerization.....	13
1.5.4 Surfactants.....	14
References	16
2. Experimental Procedures	19
2.1 Source of chemicals.....	19
2.2 Synthesis of polymers.....	24
2.2.1 Synthesis of PNIPMAM.....	24
2.2.2 Synthesis of poly(3-acrylamidopropyl) trimethylammonium chloride	24
2.2.3 Synthesis of poly(N-(3-(dimethylamino) propyl) methacrylamide) (polyDMAPMA).....	25
2.2.4 Synthesis of Poly[3-(methacryloylamino)propyl] trimethylammonium chloride (polyMAPTAC).....	25
2.2.5 Synthesis of Poly(2-dimethylaminoethylmethacrylate) (PolyMADAME)	26
2.3 Cloud point and deposition point tests	27
3. Results.....	28
4. Discussion	34
5. Conclusions.....	37

1. Introduction

1.1 Background

Gas hydrates are crystalline compounds formed as a network of hydrogen bonded water molecules and small guest molecules such as methane are included within the cavities formed by the water cage. These stable solids can be formed at temperatures up to 20 °C and pressure above 5 MPa [1]. In oil and gas fields where the production conditions reach low temperatures and high pressures, the formation of gas hydrates are unavoidable without proper treatment. With the formation of hydrates, the risk of shutdown and stop in production lines are high and could be expensive.

There are several methods for hydrate prevention, such as pipeline insulation, pressure reduction and thermodynamic hydrate inhibitor (THI) injection [2]. The use of THI for preventing pipeline blockage requires large amount of methanol or ethylene glycol (up to 40 vol%) and shift the hydrate equilibrium condition to lower temperature and higher pressure. Another type of chemical inhibitors is kinetic hydrate inhibitor (KHI) which is a type of low-dosage hydrate inhibitor (LDHI). KHIs are polymers that are used up- and downstream in oilfield operations, which delay hydrate nucleation and crystallization at low dosage around 1-2 wt% [3]. These polymers have hydrophilic and hydrophobic moieties, making them water soluble at low temperatures. When the temperature is increased, the polymer then gets cloudy and is known as the cloud point temperature (T_{cl}). If the temperature is further increased, the polymer will precipitate and deposits, which is known as the deposition temperature (T_{dp}). In this case the KHI will be ineffective and will not prevent hydrates from forming blockage in the pipeline. This issue is apparent when KHIs is injected close to the wellhead where temperatures are high, and the polymer then precipitates and deposits.

There are two suppliers of KHIs that have shown to have products that have low T_{cl} but high T_{dp} but the method is unknown. In this report the focus will be on finding a method of increasing the deposition temperature of known KHIs by addition of another more hydrophilic polymer. This second polymer may be neutral, or may have cationic or anionic functional groups. A few non-polymeric molecules were also investigated.

In this study the use of two known KHIs has been used experimentally in the lab to improve their T_{dp} by addition of other polymers. The KHIs poly(N-vinylcaprolactam) (PVCap) and poly(N-isopropylmethacrylamide) (PNIPMAM) are well known KHIs used in the upstream oil industry. The choice of KHI that is used in the field depends mostly on the performance and price of KHI. The polymers that were best at raising the deposition point of the KHI polymers have also been studied in high pressure gas hydrate equipment to see if they affect the KHI performance. A method to raise T_{dp} of PVCap and PNIPMAM is done by making a copolymer with a more hydrophilic monomer, however this method has an adverse effect on the performance of the KHI. It has been reported that adding denaturants such as urea can raise T_{dp} , making a KHI water soluble at higher temperature. The proposed mechanisms are that urea either changes the structure of water molecules making the hydrophobic groups of

the polymer more solvated, or that urea interacts with the backbone of the polymer via hydrogen-bonding and van der waals attractions making the polymer to denature. Another method to raise T_{dp} is by adding surfactants, however these methods need high concentrations of surfactants, making this method expensive.

1.2 Gas Hydrate Structure

Gas hydrates, also known as clathrate hydrates are ice-like inclusion compounds that are formed of water and small hydrocarbons. Clathrate hydrates can be formed in different crystal structures, known as structure I (SI), structure II (SII) and structure H (SH), as shown in figure 1. The structures that are formed have cavities of different sizes and accommodate one guest molecule per cavity. The most common structures are SI and SII which contain light hydrocarbons, including methane, ethane, propane, and isobutene, as well as nonpolar molecules such as carbon dioxide, nitrogen, argon, krypton and xenon [4]. Clathrate hydrates are typically comprised of 85 mol% water and 15 mol% guest molecules when all cavities are occupied [5]. Structure I and II are made of crystals that have cages 5^{12} formed as 12 planar pentagonal faces, in addition SI has cages $5^{12}6^2$ and SII contains cages $5^{12}6^4$. The formation of the different structures depends on which guest molecules there are present in the cavities [6].

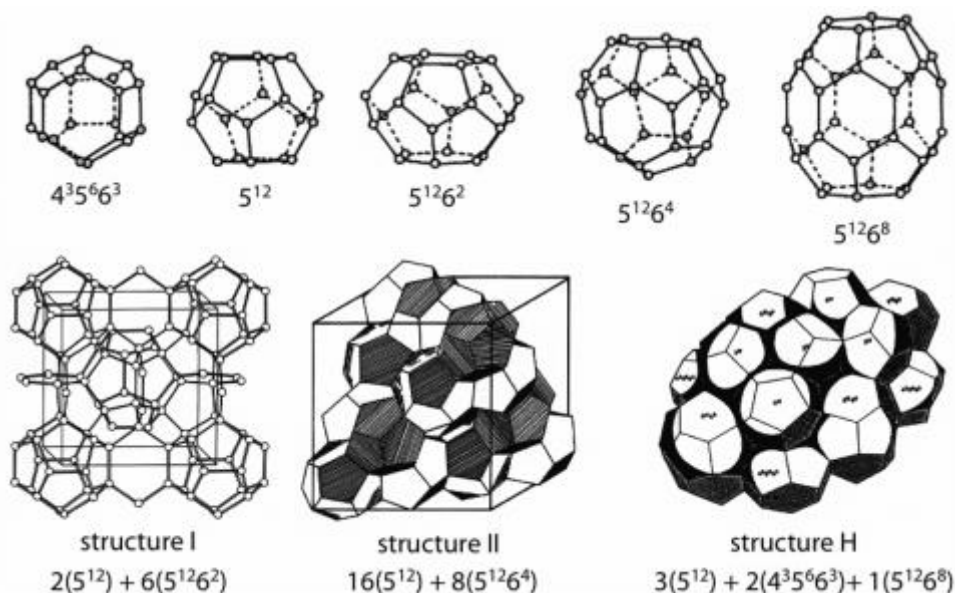


Figure 1. Crystal hydrate structures formed by water cages. The cages assemble structures SI, SII and SH[4].

1.3 Kinetic hydrate inhibitors

The first low dosage hydrate inhibitors (LDHI) products to be used in the oil and gas industry were in 1995 as a substitute for methanol and other thermodynamic hydrate inhibitors. Kinetic hydrate inhibitors (KHI) are a type of LDHI. But some countries do not allow the use of certain types of these chemicals due to their environmental properties, specifically biodegradation. Norway is one of the countries that have strict offshore regulations regarding toxicity of these chemicals. More research on KHIs are currently under development to improve the use of these inhibitors [7]. The use of KHIs to inhibit hydrate formations has been the subject of extensive study [8]. KHIs are water-soluble polymers that consist of monomers each containing hydrophobic and hydrophilic parts. These hydrophilic groups are often amides or imides which can form hydrogen bonds with the hydrates. Hydrate formation can be delayed by the increase of the energy barrier to form hydrate nucleation or adsorb to the surface of the hydrate crystals [9]. The performance of KHIs depends on several factors, such as the subcooling, gas/oil ratio and salinity. When screening the performance of a KHI, the subcooling is the most important factor to consider. The subcooling is the difference between the hydrate equilibrium temperature and the fluid temperature, which is the thermal driving force for hydrate formation. High driving force will induce hydrate nuclei in the aqueous phase which creates a surface area for the KHI to act on [10].

1.3.1 Poly(N-vinylcaprolactam) (PVCap)

The KHI of Poly(N-vinylcaprolactam) (PVCap) is made of N-vinylcaprolactam monomers and can be made in different molecular weight (M_w) and molecular weight distribution. The low M_w of this polymer gives greater inhibition performance than the high M_w polymers for SII hydrate structures. This polymer is the subject of extensive study on the effect of hydrate inhibition [11, 12]. In the case of SI hydrate structures, the high M_w of PVCap have a better inhibition performance than the low M_w [3]. PVCap have a T_{cl} of 30-40 °C in deionized water and the T_{dp} is few degrees above the T_{cl} , depending on the polymerization conditions and M_w [13]. The structure of PVCap is shown in figure 2 below. The structure of PVCap have an alkylamide included in the structure. This pendant group interacts and forms a hydrogen bonding with the hydrate surface, thus preventing hydrate formation.

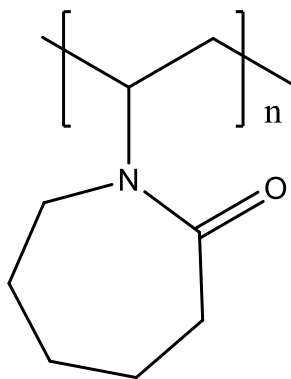


Figure 2. Poly(N-vinylcaprolactam)

1.3.2 poly(N-isopropylmethacrylamide) (PNIPMAM)

The polymer poly(N-isopropylmethacrylamide) (PNIPMAM) is used for different applications; in the biomedical industry, as “smart” gels used in robotics and photographic films [14]. This thermo-responsive polymer is also used as a KHI to prevent hydrate formation. The structure of PNIPMAM is similar to the structure of poly(N-isopropylacrylamide) (PNIPAM) where an additional methyl group is located on each monomeric unit as shown in figure 3 below. The addition of a hydrophilic group could suggest that the T_{cl} and the T_{dp} of PNIPMAM is lower than PNIPAM, but is about 13 °C higher. The cloud point of PNIPMAM is 45 °C, whereas the cloud point of PNIPAM is around 32 °C when both polymers have similar M_w [15]. The presence of a methyl group significantly increases the phase transition of this polymer compared with the PNIPAM [16].

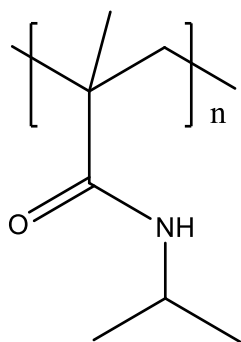


Figure 3. Poly(N-isopropylmethacrylamide)

1.4 Cloud point and deposition point

Many water-soluble polymers have a reversible phase transition in response to increase of temperature. In some literature, the T_{cl} of a KHI is referred as lower critical solution temperature (LCST) and the T_{dp} is described as coil to globule transition [17]. When a polymer is dissolved in water in a test tube and the mixture is heated, the phase transition is visible when the color changes from clear to opaque or hazy. If the solution is further heated, the polymer then precipitates and deposits. The deposition of the polymer can be seen when white clumps deposits on the surface of the test tube. A method to determine the T_{cl} and T_{dp} is by using a thermometer in a solution of a dissolved polymer and carefully heating while stirring. Another method to determine the cloud point of a KHI is by using dynamic light scattering measurements, a sample is heated at a constant rate and measure the turbidity of the solution. When the solution turns cloudy, the intensity of scattered light increases, and the cloud point of the polymer is determined [18]. The figure below shows a samples of the polymer PNIPMAM that is dissolved in water and heated. The solution to the left contains the polymer dissolved at room temperature, the test tube in the middle shows when the cloud point is reached, and the test tube to the right shows the deposition point of the polymer. As mentioned, this process is reversible if the temperature is decreased, the polymer then dissolves, and the color becomes clear again. The ability of the polymer to remain dissolved depends on the hydrophilic groups of the polymer. The increase in entropy upon heating is the driving force behind the phase transition due to loss of hydration of the hydrophilic group and the hydrophobic interaction of the alkyl group becomes more dominant [19].

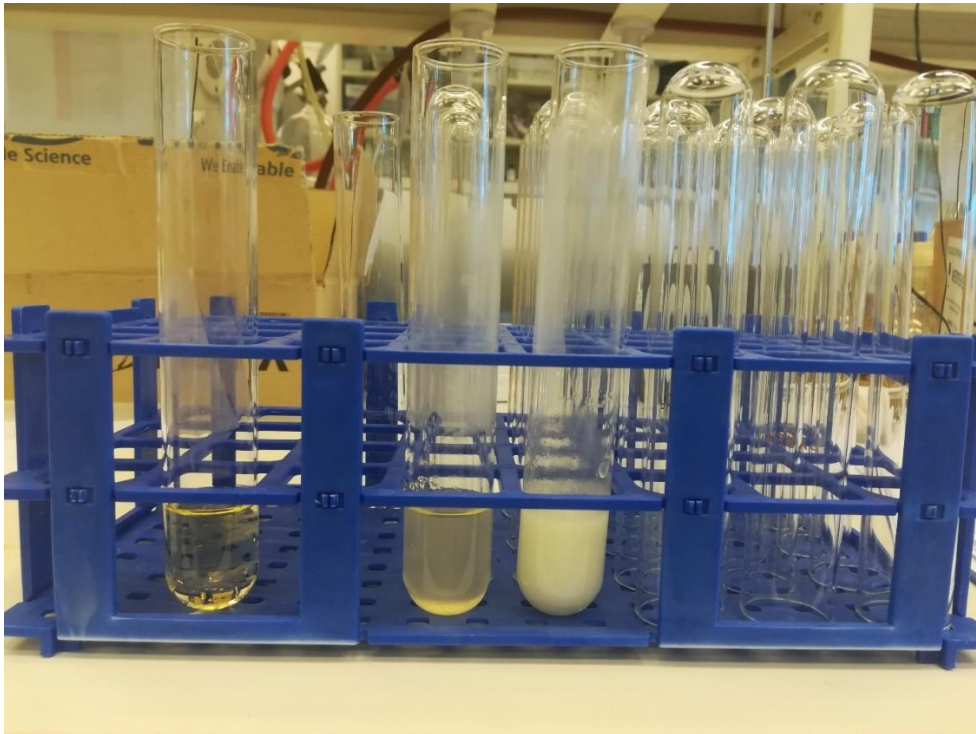


Figure 4. Samples of PNIPMAM dissolved in water. On the left the solution at room temperature, in the middle when the cloud point is reached, and the deposition point on the right test tube.

1.5 Methods to raise cloud point and deposition point

There have been several studies into methods to raise the cloud point of polymers using salts, denaturing agents, surfactants or by copolymerization. These methods could have a useful effect on the cloud point and deposition point of KHIs, but there is a concern on the performance of the KHIs when these methods are used. The amounts of chemicals needed to improve the T_{cl} and T_{dp} is also a factor to be considered. The price of certain chemicals can be very expensive and not economically viable. The use of surfactants or denaturing agents requires large amounts of chemicals if they are considered to be used in the field, making them too expensive for the company.

1.5.1 Salt and Hofmeister series

Franz Hofmeister first discovered that additions of salts lead to rapid precipitation of proteins from egg white. This effect of salts on proteins is known as “salting-out” and is referred to the decrease in solubility of a nonelectrolyte with increasing concentration of electrolyte. The Hofmeister effect have an impact on range of phenomena, such as protein folding, solubility of charged molecules, cloud point and phase separation [20]. The ability of ions to precipitate proteins is ordered in what is known as the Hofmeister series. Table 1 shows the sequence of anions and cations with respect to their ability to precipitate proteins in aqueous solution. An interesting aspect of the Hofmeister series is that anions have more effect than that of cations [21].

Table 1. Hofmeister series [22].

Anions	$SO_4^{2-} > HPO_4^{2-} > CH_3COO^- > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$
Cations	$Mg^{2+} > Li^+ > Na^+ > K^+ > NH_4^+ > (CH_3)_4N^+$

The addition of salts such as Na_2SO_4 , K_2SO_4 and $NaCl$ decreases the cloud point of polymers linearly with increasing concentration of salt. Other salts such as $NaNO_3$ can increase the cloud point of a polymer in small concentrations, but decrease the cloud point at higher concentrations [23]. A study on the effect of salts on the cloud point of PNIPAM have shown that the effects of ions follow the Hofmeister series. A solution of 1,4 wt% PNIPAM in 1M $NaCl$, $NaBr$, NaI and KCl was found to decrease the cloud point to 20, 25, 30 and 19 °C respectively, from the cloud point of 32 °C in pure water. This study showed that salts interact with the amide group of the polymer thus effecting the protein stability [24]. Another theory suggest that ions can interact with water molecules and effect the formation of gas hydrates. The addition of $NaCl$ to a CO_2 -hydrate forming system inhibits the hydrate formation thermodynamically. At concentration up to 20 wt% $NaCl$, the temperature of gas hydrate

formation was lowered by 12 °C [25]. The presence of ions in seawater and produced water have an impact on the cloud point and deposition point of KHIs. In most cases the ions will lower the T_{cl} and T_{dp} , but at the right concentrations of salts the T_{cl} and T_{dp} can increase by a few degrees.

1.5.2 Denaturing agents

Denaturing agents is commonly used to alter the effect of polymer folding and stabilize proteins in biochemistry and the pharmaceutical industry. Examples of denaturing agents are guanidine salt, urea and thiourea. The effect of denaturing agents can in some cases elevate the cloud point and in other cases lower the cloud point and deposition point of a polymer [26]. The molecular mechanisms of the denaturing agents are still not fully understood, but there have been proposed two distinct mechanisms. The first one is the “indirect mechanism” where the urea changes the structure of water molecules making the hydrophobic groups of the polymer more solvated. The other is the “direct mechanism” where urea interacts with the backbone and/or side groups of the polymer by hydrogen bonding, other electrostatic interaction and van der waals attractions causing the polymer to denature. A study on methylated urea have shown a better effect than that of urea, with regard to the deposition point of a solution containing a KHI of PNIPAM [27]. The effect of tetramethylurea (TMU) decreases the enthalpy change of the solution with increasing concentration of the denaturing agent. The presence of a more hydrophobic methyl groups as shown in the figure 5, causes stronger van der waals interaction with the hydrophobic isopropyl groups of PNIPAM. This in turn causes the weakening of the polymers hydrophobic interaction thus increasing the phase transition temperature.

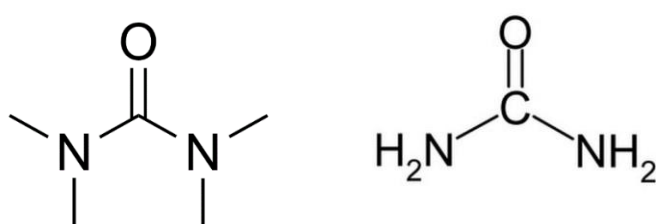


Figure 5. Tetramethylurea (TMU) on the left side and urea on the right side.

Another commonly used denaturing agent is guanidinium salts. The unique molecular structure of guanidinium (Gnd^+) with flat hydrophobic faces makes it capable of hydrogen bonding by its three NH_2 groups, as shown in figure 6. Typically, guanidinium salts are formed with a weaker hydrated counter-anions, such as $GndSCN$ and $GndCl$. The anions can in this case effect the solubility of polymers because of the Hofmeister effect. A study on the effect of different guanidinium salts on the T_{cl} of a solution with polypeptide shows that the

anions followed the Hofmeister series. The cloud point of the polymer decreased with the addition of salt concentrations below 0.5 M in the following order: $\text{GndSCN} > \text{Gnd}_2\text{SO}_4 > \text{GndCO}_3 > \text{GndNO}_3$ [28]. When the salt concentration of GndSCN was higher than 1.0 M, the cloud point of the polymer turned and began to increase. The addition of GndCl increased the cloud point with increasing concentrations. The hydrophobic groups of Gnd^+ interacts with the hydrophobic backbone of the polymer, but this interaction is weak and are dictated by the nature of the counterion. When Gnd^+ is paired with a more weakly hydrated anion, such as SCN^- , the interaction of the anion with the amide group helps the polymer to stabilize.

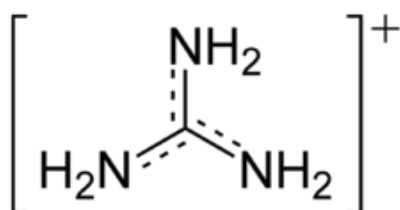


Figure 6. guanidinium.

There are a few known chemicals that can counteract the denaturing effect of substances such as urea. Trimethylamine-N-oxide (TMAO) is a classic example [29]. One computer modelling report indicates that TMAO can increase the solubility of hydrophobic molecules in water[30]. This might be detrimental, raising the concentration of dissolved hydrate-forming gases, promoting hydrate nucleation. Thus, TMAO has counteracting effects. On the one hand, TMAO could be useful to improve the polymer solubility but it could lead to lower KHI performance. Another study reports that TMAO achieves its protein-stabilizing ability through the combination of (at least) two mechanisms: (i) It decreases the hydrogen bonding ability of water and hence the stability of the unfolded state, and (ii) it acts as a molecular crowder, as suggested by a recent computational study, that can increase the stability of the folded state via the excluded volume effect [31]. Another study suggests that the effect of TMAO to counteract denaturing may be due to the ability of the amine oxide to hydrogen-bond with $-\text{NH}-$ groups in proteins [32].

1.5.3 Copolymerization

A method to increase the cloud point and deposition point of a KHI is by copolymerization. There have been several studies that have been done on the effect of copolymerization of a known KHI, such as PNIPMAM [33, 34]. In one of the studies, the synthesis and performance testing of a copolymer of poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) was characterized and analyzed. The synthesis was done by using high throughput (HTP) material synthesis to create detailed structure of the copolymer and post synthetic modification was carried to accurately control the polymer with similar molecular weight, M_w

distribution, end groups and composition along the chain [35]. In general, the increase of the hydrophobic alkyl chain length lowers the cloud point of a polymer. But in this case the increase of hydrophobic alkyl chain resulted in higher cloud point. The PNIPAM-co-AA with low molecular weight had higher cloud point than that of the polymers with higher molecular weight. One of the tested copolymers had a cloud point of 83 °C in water and showed to have strong hydrate inhibition. In some cases, the use of copolymerization is used as a method to modify the KHI to be compatible with corrosion inhibitors. One study showed that the copolymers of PVCap can be used with a corrosion inhibitor with little effect on KHI performance [36].

In another study, the copolymer of PNIPAM and (N,N-dimethylhydrazidoacrylamide) (DMHAM) was examined and the target was to synthesize a copolymer that had a cloud point higher than the homo polymer of PNIPAM. The aim was to modify the polymer with a more hydrophilic monomer which also had similar molecular structure. The difference in the structure was the -CH- group in the isopropyl groups that was replaced with a tertiary nitrogen atom. The starting material that are used to make the DMHAM side chain is a cheap and commercially available chemical used in rocket fuels [37]. These copolymers were tested in a high-pressure gas hydrate rocker rig equipment to screen the performance of the polymers as KHIs. The synthesized copolymers showed to have high cloud points in both deionized water and in NaCl solution. A copolymer 1:2 of DMHAM/NIPAM had a cloud point of 58 °C in deionized water and had the highest performance for this class of copolymers. Another copolymer that showed high cloud point, was the 1:1 copolymer of DMHAM/NIPAM, with cloud point of 83 °C in 3.6% NaCl solution and no cloud point in deionized water, but the performance was reduced compared with other copolymers. The same research team also examined the possibility of raising the cloud point of the KHI PVCap. The synthesis of a copolymers with DMHAM monomer was carried and the performance of the KHI was tested in the same matter. The copolymer 1:2 DMHAM/VCap had a cloud point of 50 °C in deionized water and gave the best KHI performance for this class of copolymers. The copolymer of 1:1 DMHAM/VCap had no cloud point up to 100 °C in both deionized water and with high salt solution, and it gave excellent KHI performance at pH 5 [13].

1.5.4 Surfactants

The interaction of surfactants and water-soluble polymer have been extensively studied due to their interesting properties and important applications in detergency, pharmaceuticals, enhanced oil recovery, paint and coating. The use of surfactants can also be used to elevate the cloud point of temperature responsive polymers [38]. Sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) are examples of surfactants that can be used with KHIs to increase the cloud point and the deposition point of the polymers. A study on the effect of SDS and DTAB on a solution containing the polymer of PVCap in 0.01 M NaCl

solution shows to increase the cloud point [39]. The increase in cloud point was first observed when the concentration of SDS was at 0.5 mM and sharply increased with increasing concentration. The concentration of DTAB was 12 mM when the cloud point began to increase and was further elevated with increasing concentration. In this case the anionic surfactant SDS had greater effect on the cloud point compared with the cationic surfactant DTAB. This indicates that the critical micelle concentration (cmc) of DTAB was 12 mM and in that concentration the micelles of DTAB started to interact with PVCap. On the other hand, the cmc of SDS was 0.5 mM and above this concentration the SDS micelles binds to the polymer. It was presumed that the difference in the binding of SDS and DTAB with the polymer is that the weaker interaction of the shielded trimethylammonium group of DTAB with the amide compared with the binding of SDS with the two hydrophobic alkyl chains. The interaction of SDS and PVCap involves hydrophobic forces and with the possible formation of hydrophobic clusters of SDS molecules along the polymer chain.

In another study of the behavior of polymers when surfactants are added, the use of SDS and cetylpyridinium chloride (CPS) also confirms the increase of the phase transition temperature of PVCap when small concentrations of surfactants are added. This effect contributed to the change of the hydrophilic-hydrophobic balance of PVCap due to the adsorption of ionic surfactant and the transformation of neutral polymer to polyelectrolyte. The second factor that prevents macromolecular aggregation, is the repulsion of similar charged particles formed when PVCap and the surfactant interacts together [40]. By adding ionic surfactant, the shift of the collapse transition temperature is increased to a higher temperature region, this means that both the cloud point temperature and the deposition temperature is elevated when these ionic surfactants are used. The concern is the adverse effect on the KHI performance when surfactants is used in combination with a KHI. It is important to carefully examine the performance of the KHI in the lab to test the hydrate inhibition of the KHI when a surfactant is added.

References

1. Akhflash, M., et al., *Gas Hydrate Thermodynamic Inhibition with MDEA for Reduced MEG Circulation*. Journal of Chemical and Engineering Data, 2017. **62**(9): p. 2578-2583.
2. Ding, L., et al., *Hydrate Deposition on Cold Pipe Walls in Water-in-Oil (W/O) Emulsion Systems*. Energy and Fuels, 2017. **31**(9): p. 8865-8876.
3. Seo, S.D., et al., *Effects of Poly(N-vinylcaprolactam) Molecular Weight and Molecular Weight Distribution on Methane Hydrate Formation*. Energy & Fuels, 2017. **31**(6): p. 6358-6363.
4. Sum, A.K., C.A. Koh, and E.D. Sloan, *Clathrate hydrates: From laboratory science to engineering practice*. Industrial and Engineering Chemistry Research, 2009. **48**(16): p. 7457-7465.
5. Sloan, E.D., *Fundamental principles and applications of natural gas hydrates*. Nature, 2003. **426**(6964): p. 353-363.
6. Walsh, M.R., et al., *Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth*. Science, 2009. **326**(5956): p. 1095-1098.
7. Kondapi, P. and R. Moe, *Today's Top 30 Flow Assurance Technologies: Where Do They Stand?* 2013, Offshore Technology Conference: Huston Texas.
8. Hong, S.Y., et al., *Kinetic Studies on Methane Hydrate Formation in the Presence of Kinetic Inhibitor via in Situ Raman Spectroscopy*. Energy & Fuels, 2012. **26**(11): p. 7045-7050.
9. Kelland, M.A., *Production Chemicals for the Oil and Gas Industry*. 1 ed. 2009.
10. Park, J., et al., *Performance of Poly(N-isopropylacrylamide)-Based Kinetic Hydrate Inhibitors for Nucleation and Growth of Natural Gas Hydrates*. Energy & Fuels, 2017. **31**(3): p. 2697-2704.
11. Gulbrandsen, A.C. and T.M. Svartas, *Effects of PVCap on Gas Hydrate Dissociation Kinetics and the Thermodynamic Stability of the Hydrates*. Energy & Fuels, 2017. **31**(9): p. 9863-9873.
12. Cortez-Lemus, N.A. and A. Licea-Claverie, *Poly(N-vinylcaprolactam), a comprehensive review on a thermoresponsive polymer becoming popular*. Progress in Polymer Science, 2016. **53**: p. 1-51.
13. Mady, M.F. and M.A. Kelland, *N,N-Dimethylhydrazidoacrylamides. Part 2: High-Cloud-Point Kinetic Hydrate Inhibitor Copolymers with N-Vinylcaprolactam and Effect of pH on Performance*. Energy & Fuels, 2015. **29**(2): p. 678-685.
14. Djokpe, E. and W. Vogt, *N-isopropylacrylamide and N-isopropylmethacrylamide: Cloud points of mixtures and copolymers*. Macromolecular Chemistry and Physics, 2001. **202**(5): p. 750-757.
15. Tang, Y.C., Y.W. Ding, and G.Z. Zhang, *Role of methyl in the phase transition of poly(N-isopropylmethacrylamide)*. Journal of Physical Chemistry B, 2008. **112**(29): p. 8447-8451.
16. Dybal, J., M. Trchova, and P. Schmidt, *The role of water in structural changes of poly(N-isopropylacrylamide) and poly(N-isopropylmethacrylamide) studied by FTIR, Raman spectroscopy and quantum chemical calculations*. Vibrational Spectroscopy, 2009. **51**(1): p. 44-51.
17. Kirpach, A. and D. Adolf, *High pressure induced coil-globule transitions of smart polymers*. Macromolecular Symposia, 2006. **237**: p. 7-17.
18. Laukkanen, A., et al., *Formation of colloiddally stable phase separated poly(N-vinylcaprolactam) in water: A study by dynamic light scattering, microcalorimetry, and pressure perturbation calorimetry*. Macromolecules, 2004. **37**(6): p. 2268-2274.
19. Rathfon, J.M. and G.N. Tew, *Synthesis of thermoresponsive poly(N-isopropylmethacrylamide) and poly(acrylic acid) block copolymers via post-functionalization of poly(N-methacryloxysuccinimide)*. Polymer, 2008. **49**(7): p. 1761-1769.
20. Hashemi, M. and T.G. Chasteen, *Hofmeister effect challenge*. Analytical and Bioanalytical Chemistry, 2011. **400**(3): p. 643-644.

21. Cooper, R.J., et al., *Hydration of Guanidinium: Second Shell Formation at Small Cluster Size*. Journal of Physical Chemistry A, 2014. **118**(30): p. 5657-5666.
22. Domâinguez de Marâia, P., P. Domâinguez de Marâia, and P. Domínguez de María, *Ionic Liquids in Biotransformations and Organocatalysis : Solvents and Beyond*. Ionic Liquids in Biotransformations and Organocatalysis: Solvents and Beyond. 2012, Hoboken: Wiley.
23. Mori, T., et al., *Thermosensitive copolymers having soluble and insoluble monomer units, poly(N-vinylacetamide-co-methyl acrylate)s: Effect of additives on their lower critical solution temperatures*. Journal of Polymer Science Part a-Polymer Chemistry, 2004. **42**(11): p. 2651-2658.
24. Du, H.B., R. Wickramasinghe, and X.H. Qian, *Effects of Salt on the Lower Critical Solution Temperature of Poly (N-Isopropylacrylamide)*. Journal of Physical Chemistry B, 2010. **114**(49): p. 16594-16604.
25. Holzammer, C., et al., *How Sodium Chloride Salt Inhibits the Formation of CO₂ Gas Hydrates*. Journal of Physical Chemistry B, 2016. **120**(9): p. 2452-2459.
26. Wang, J., et al., *Effect of Urea on Phase Transition of Poly(N-isopropylacrylamide) and Poly(N,N-diethylacrylamide) Hydrogels: A Clue for Urea-Induced Denaturation*. Macromolecules, 2016. **49**(1): p. 234-243.
27. Gao, Y.T., et al., *Insight into the Effect of Methylated Urea on the Phase Transition of Aqueous Solutions of Poly(N-isopropylacrylamide) by Microcalorimetry: Hydrogen Bonding and van der Waals Interactions*. Journal of Polymer Science Part B-Polymer Physics, 2016. **54**(12): p. 1145-1151.
28. Heyda, J., et al., *Guanidinium can both Cause and Prevent the Hydrophobic Collapse of Biomacromolecules*. Journal of the American Chemical Society, 2017. **139**(2): p. 863-870.
29. Athawale, M.V., J.S. Dordick, and S. Garde, *Osmolyte trimethylamine-N-oxide does not affect the strength of hydrophobic interactions: Origin of osmolyte compatibility*. Biophysical Journal, 2005. **89**(2): p. 858-866.
30. Sarma, R. and S. Paul, *Hydrophobic interactions in presence of osmolytes urea and trimethylamine-N-oxide*. Journal of Chemical Physics, 2011. **135**(17): p. 13.
31. Ma, J., I.M. Pazos, and F. Gai, *Microscopic insights into the protein-stabilizing effect of trimethylamine N-oxide (TMAO)*. Proceedings of the National Academy of Sciences of the United States of America, 2014. **111**(23): p. 8476-8481.
32. Venkatesu, P., M.J. Lee, and H.M. Lin, *Osmolyte Counteracts Urea-Induced Denaturation of alpha-Chymotrypsin*. Journal of Physical Chemistry B, 2009. **113**(15): p. 5327-5338.
33. Vishnevetskaya, N.S., et al., *"Schizophrenic" Micelles from Doubly Thermoresponsive Polysulfobetaine-b-poly(N-isopropylmethacrylamide) Diblock Copolymers*. Macromolecules, 2017. **50**(10): p. 3985-3999.
34. Wu, Y.D., et al., *Behavior of Temperature-Responsive Copolymer Microgels at the Oil/Water Interface*. Langmuir, 2014. **30**(26): p. 7660-7669.
35. da Silveira, K.C., et al., *High throughput synthesis and characterization of PNIPAM-based kinetic hydrate inhibitors*. Fuel, 2017. **188**: p. 522-529.
36. Park, J., et al., *Kinetic Hydrate Inhibition Performance of Poly(vinyl caprolactam) Modified with Corrosion Inhibitor Groups*. Energy & Fuels, 2017. **31**(9): p. 9363-9373.
37. Mady, M.F. and M.A. Kelland, *N,N-Dimethylhydrazidoacrylamides. Part 1: Copolymers with N-Isopropylacrylamide as Novel High-Cloud-Point Kinetic Hydrate Inhibitors*. Energy & Fuels, 2014. **28**(9): p. 5714-5720.
38. Guo, Y., et al., *A thermo-sensitive OEGMA-based polymer: synthesis, characterization and interactions with surfactants in aqueous solutions with and without salt*. Colloid and Polymer Science, 2017. **295**(2): p. 327-340.
39. Qiu, Q., P. Somasundaran, and B.A. Pethica, *Hydrophobic complexation of poly(vinyl caprolactam) with sodium dodecyl sulfate and dodecyltrimethylammonium bromide in solution*. Langmuir, 2002. **18**(9): p. 3482-3486.

40. Makhaeva, E.E., H. Tenhu, and A.R. Khokhlov, *Conformational changes of poly(vinylcaprolactam) macromolecules and their complexes with ionic surfactants in aqueous solution*. *Macromolecules*, 1998. **31**(18): p. 6112-6118.
41. Chua, P.C. and M.A. Kelland, *Poly(N-vinyl azacyclooctanone): A More Powerful Structure II Kinetic Hydrate Inhibitor than Poly(N-vinyl caprolactam)*. *Energy & Fuels*, 2012. **26**(7): p. 4481-4485.

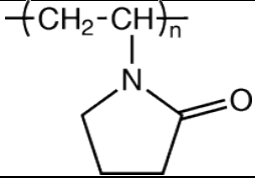
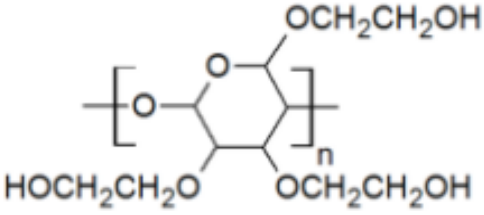
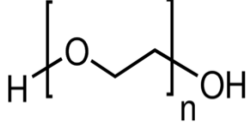
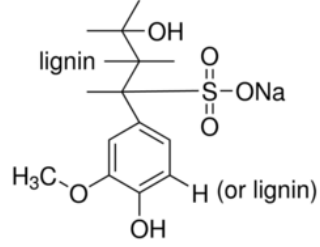
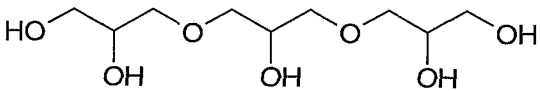
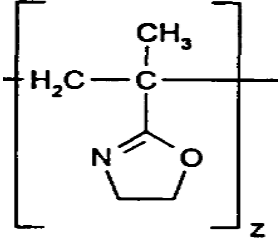
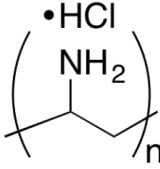
2. Experimental Procedures

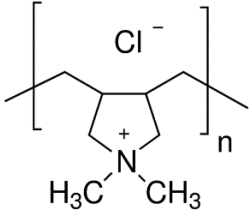
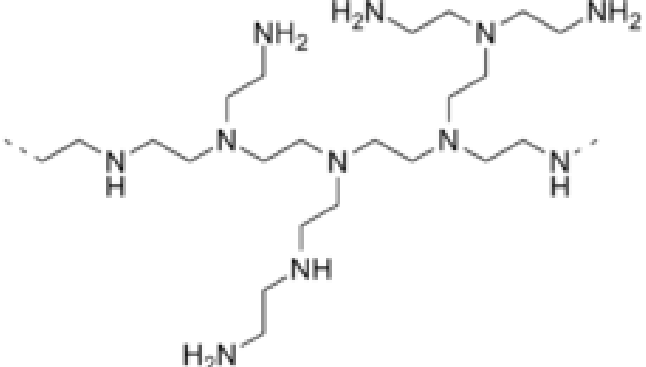
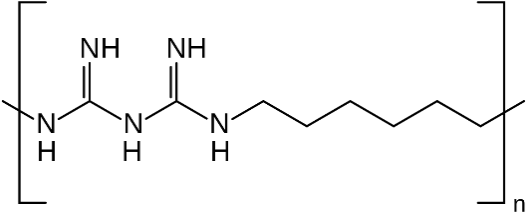
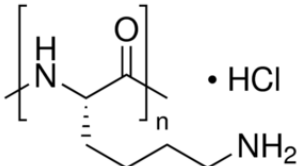
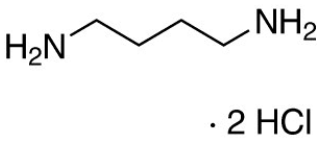
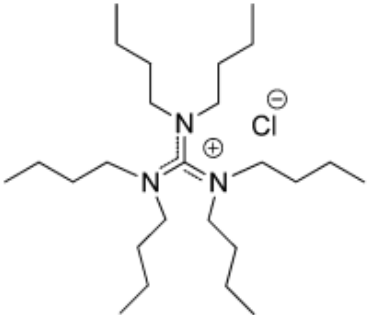
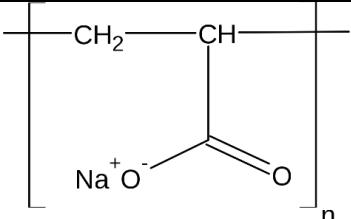
The chemicals that was used in laboratory experiments was either bought or made in the lab. Some of the polymers that was synthesized from monomers, other polymers were only protonated by adding HCl to the polymer and several chemicals was made in house. Poly(Nvinylcaprolactam), Luvicap EG is provided by BASAF and was one of two KHIs that was studied to increase the T_{dp} of the polymer by adding other polymers. The other KHI that was used is poly(N-isopropylmethacrylamide) (PNIPMAM) which were synthesized from the monomer of N-isopropylmethacrylamide provided by VISOMER. These two KHIs were the subject of extensive trials to examine the effect on the deposition point when adding non-ionic polymers, anionic polymers and cationic polymers.

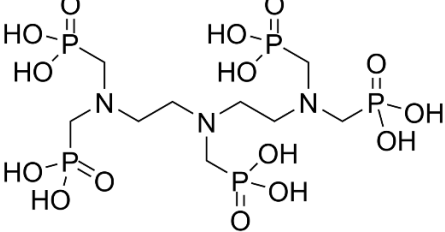
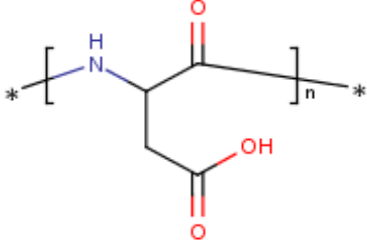
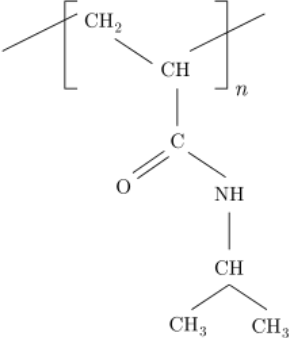
2.1 Source of chemicals

The following chemicals was bought and used in the laboratory experiments and their structures are shown in the table 2. Polyvinylpyrrolidone (PVP) 15K with $M_w = 9000$ that is provided by Ashland. Hydroxyethylcellusoe (HEC) with $M_w = 100000$ was provided by Hercules. Poly(ethylene glycol) (PEG) with $M_w = 100000$ was supplied by Aldrich. Lignosulfonate was also provided by Aldrich. Polyglycerol-3 is supplied by Solvay. Polyvinylamine (LUPAMIN 1595) with low M_w and in a solution of 15 wt% in HCl was provided by BASF. Polyvinylamine (LUPAMIN 9595) with high M_w and in a solution of 15 wt% in HCl is also provided by BASF. Poly(diallyldimethylammonium chloride) with low M_w and 35 wt% in H_2O made by Aldrich. The hyper branched polyethylenimine (HPEI) with low M_w and in a solution of 50 wt% in H_2O provided by Aldrich. Polyhexanide (COSMOCIL CQ) in a solution of 20.0 wt% was supplied by Arch. Polylysine with 50wt% provided from Chisso corporation. 1,4-diaminobutane dihydrochloride is provided by Merck. Hexa-n-butylguanidinium chloride in a solution of 70.0 wt% in H_2O provided by ECO inhibitors. Polyacrylate Sokalan PA 20 in a solution of 45 wt% was supplied by BASF. Polyoxazoline sold as EPOCROS WS-300 from Nippon Shokubai. Diethylenetriamine penta(methylenepospinic acid) (DETPMP) in a solution of 50 wt% provided by Thermphos. Polyaspartate (B-3D) 37 wt% supplied by Nanochem solutions. polyacryloylpyrrolidine (Fx-AP-1000) is supplied by Nippon Shokubai. Poly(N-vinylisobutyramide) is provided by Polymer source. The solvent 2-butoxyethanol is supplied by ACROS organics, and the solvent diethylglycolmonoethylether (DEGME) is provided by Merk. poly(N-isopropylmethacrylamide) is provided by Nippon Shokubai as Fx-AAM-IP 1000-11 with M_w of 210000.

Table 2. Structure of polymers.

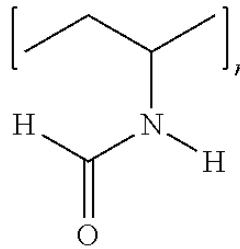
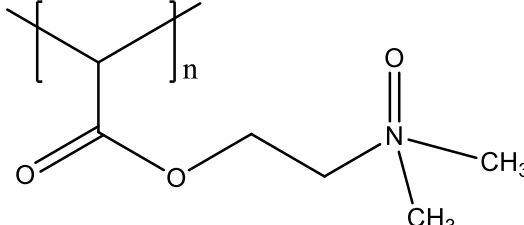
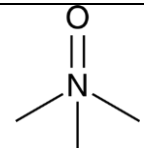
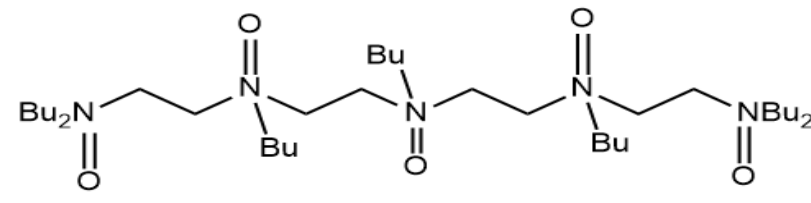
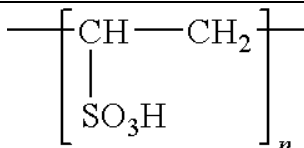
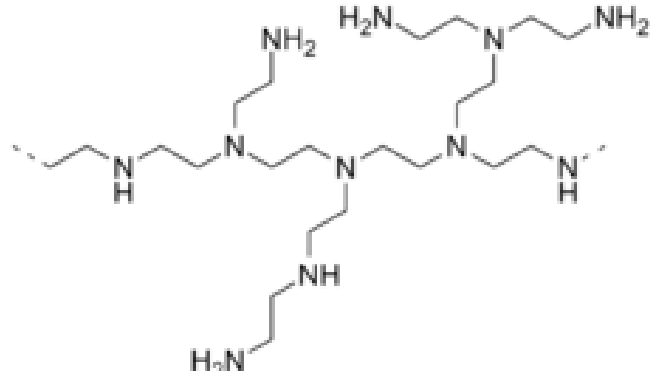
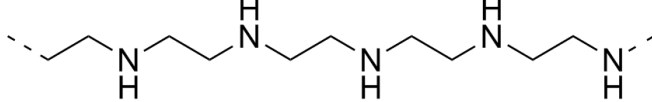
Polyvinylpyrrolidone (PVP)	$\left(\text{CH}_2 - \underset{\substack{ \\ \text{N} \\ \\ \text{C}=\text{O}}}{\text{C}} \right)_n$ 
Hydroxyethylcellulose (HEC)	
Poly(ethylene glycol) (PEG)	$\text{H} - \left[\text{O} - \text{CH}_2 - \text{CH}_2 \right]_n - \text{OH}$ 
Lignosulfonate	
Polyglycerol-3	$\text{HO} - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{O} - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{O} - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{OH}$ 
Polyoxazoline	$\left[\text{H}_2\text{C} - \underset{\substack{ \\ \text{CH}_3 \\ \\ \text{N} \\ \\ \text{O}}}{\text{C}} \right]_z$ 
Polyvinylamine	$\left(\text{CH}_2 - \underset{\substack{ \\ \text{NH}_2}}{\text{C}} \right)_n \cdot \text{HCl}$ 

Poly(diallyldimethylammonium chloride)	
Hyperbranched Polyethyleneimine (HPEI)	
Polyhexanide	
Polylysine.HCl	
1,4-diaminobutane dihydrochloride	
Hexa-n-butylguanidinium chloride	
Polyacrylate	

Diethylenetriamine penta(methylenephosphinic acid)	
Polyaspartate	
poly(N-isopropylmethacrylamide)	

The following chemicals were made in house and their structures are shown in table 3. Polyvinylformamide made in solution of 10.0 wt% in H₂O. Poly(dimethylamine oxide)ethylacrylate is made in a solution of 21.4 wt% in H₂O. Trimethylamine oxide is made as 27.6 wt% solution in H₂O. Tetraethylenepentamine polybutylated amine oxide (TEPA-Bu-AO) in a solution of 35.1 wt% in H₂O. Polyvinylsulfonate made as 30 wt% in HCl with pH 4 and M_w = 3000. The polymers that was protonated with HCl is polyethylenimine, the hyper branched polymer (HPEI) 27,7 wt% 2:1 in HCl with low M_w, polyethylenimine hyper branched polymer (HPEI) 29,3 wt% 1:1 in HCl with low M_w, polyethylenimine 17,5 wt%, made of linear polyethylenimine (LPEI) with pH 3-4 supplied from polysciences with M_w of 2500 and polyethylenimine 17,5 wt% also made from linear polyethylenimine (LPEI) with pH of 3-4 provided by polysciences with M_w of 25000. The polymer polyt-butylmethacrylamide and poly(N,N-diethylacrylamide) is made in house.

Table 3. Structure of polymers

Polyvinylformamide	
Poly(dimethylamine oxide)ethylacrylate	
Trimethylamine oxide	
TEPA-Bu-AO	
Polyvinylsulfonate	
Hyperbranched Polyethylenimine (HPEI)	
Linear Polyethyleneimine (LPEI)	

2.2 Synthesis of polymers

Several polymers were synthesized in the laboratory and used in the experimental trials. The polymers were synthesized using a catalyst and monomers that was heated for 12 hours. The chemicals used to synthesize the polymers are: N-isopropylmethacrylamide is supplied by VISOMER, (3-acrylamidopropyl) trimethylammonium chloride 17.5 wt% in H₂O provided by Aldrich, N-(3-(dimethylamino)propyl) methacrylamide provided by VISIOMER, [3-(methacryloylamino)propyl)] trimethylammonium chloride provided by Aldrich as 50 wt% solution in H₂O, 2-dimethylaminoethylmethacrylate provided by VISIOMER.

2.2.1 Synthesis of PNIPMAM

5.0 grams of the monomer N-isopropylmethacrylamide was weight and placed in a round-bottom flask. 0.052 grams (1wt%) of the catalyst azobisisobutyronitril (AIBN) was added and 20 ml of 2-propanol was used as the solvent for the reaction. A magnetic stirring bar was placed in the flask and then the flask was connected to a tube that can flush the air out with N₂. The air was then flushed out 4 times to make sure that the reaction is done under N₂, without any air inside the flask. The solution was then heated to 80 °C while stirring and left for 12 hours so that the monomer can polymerize. The solvent is then evaporated under vacuum in the evaporator apparatus until all the solvent is removed. The product that was produced from the reaction was a crystal solid with pale yellow color. The product was then weight and transferred to a container. The structure of PNIPMAM is shown in figure 3 in section 1.3.2.

2.2.2 Synthesis of poly(3-acrylamidopropyl) trimethylammonium chloride

1.0 grams of the monomer (3-acrylamidopropyl) trimethylammonium chloride was weight and transferred to a round-bottom flask. 0.010 grams (1wt%) of the catalyst 2,2 azobis(2-methylpropionamide) dihydrochloride was added and 15 ml of deionized water was used as the solvent for the reaction. The same procedure was followed as described in 2.2.1. The solvent is then evaporated under vacuum in the evaporator apparatus until all the water is removed. The product that was produced from the reaction was a viscous solution with pale brown color. The product was then weight and transferred to a container. The structure of the polymer is shown in figure 7.

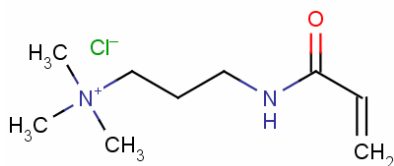


Figure 7. poly(3-acrylamidopropyl) trimethylammonium chloride.

2.2.3 Synthesis of poly(N-(3-(dimethylamino) propyl) methacrylamide) (polyDMAPMA)

5.0 grams of the monomer N-(3-(dimethylamino)propyl) methacrylamide was weighed and transferred to a round-bottom flask. 0.050 grams (1wt%) of the catalyst AIBN was added and 15 ml of 2-propanol was used as the solvent for the reaction. The same procedure was followed as described in 2.2.1. The solvent is then evaporated under vacuum in the evaporator apparatus until all the solvent is removed. The product that was produced from the reaction was a crystal solid with white color. The product was then weighed, and the yield was 3.13 g of polymer. The produced polymer was then transferred to a container. -the structure of the polymer is shown in figure 8

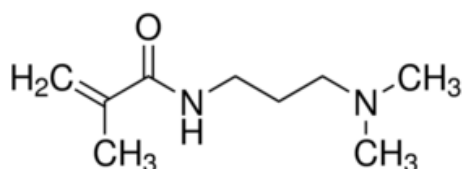


Figure 8. poly(N-(3-(dimethylamino) propyl) methacrylamide)

2.2.4 Synthesis of Poly[3-(methacryloylamino)propyl] trimethylammonium chloride (polyMAPTAC)

10.0 grams of the monomer [3-(methacryloylamino)propyl] trimethylammonium chloride was weighed and transferred to a round-bottom flask. 0.050 grams (1wt%) of the catalyst 2,2 azobis(2-methylpropionamide) dihydrochloride was added and 15 ml of deionized water was used as the solvent for the reaction. The same procedure was followed as described in 2.2.1. The solvent is then evaporated under vacuum in the evaporator apparatus until all the water is removed. The product that was produced from the reaction was a viscous transparent

solution that was diluted to 17.5 wt% solution in H₂O and transferred to a container. The structure of the polymer is shown in figure 9.

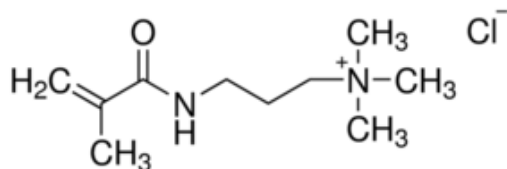


Figure 9. Poly[3-(methacryloylamino)propyl] trimethylammonium chloride.

2.2.5 Synthesis of Poly(2-dimethylaminoethylmethacrylate) (PolyMADAME)

5.05 grams of the monomer N-(3-(dimethylamino)propyl) methacrylamide was weighed and transferred to a round-bottom flask. 0.050 grams (1wt%) of the catalyst AIBN was added and 15 ml of 2-propanol was used as the solvent for the reaction. The same procedure was followed as described in 2.2.1. The solvent is then evaporated under vacuum in the evaporator apparatus until all the solvent is removed. The product that was produced from the reaction was a viscous and transparent solution. The product was then weighed, and the yield was 4.03 g and polymer were then transferred to a container. The structure of the polymer is shown in figure 10.

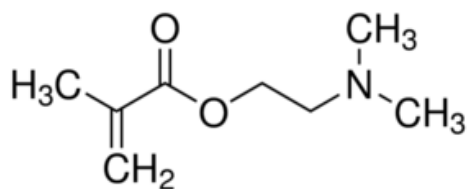


Figure 10. Poly(2-dimethylaminoethylmethacrylate).

2.3 Cloud point and deposition point tests

Several tests were done to determine the cloud point (T_{cl}) and deposition point (T_{dp}) of the KHIs PVCap and PNIPMAM in combination with other polymers and in different concentration. The chosen concentration of the KHI is always less than 1 wt%, the reason is that the use of KHIs in the field usually requires less than 1 wt% of the KHI and often the concentration is only 0.5 wt% or even 0.25 wt%. The KHI was first weight in a sample glass then dissolved in deionized water to make the required concentration. Then the other polymer was weight and added to the solution and then dissolved into the solution. Then the solution is then transferred to a test tube. A thermometer is placed into the test tube and the solution is then heated carefully with a hot air gun while stirring the test tube. When the solution gets cloudy, the temperature is noted, and the solution is heated further until the polymer deposits on the wall of the test tube. Sometimes the T_{dp} is not observed when reaching temperature above 90 °C, the solution then starts boiling and the T_{dp} is then noted to be >90 °C. This procedure was repeated for each test with the different combination of polymers. The same procedure was also followed when a brine solution with 3.5 wt% NaCl was used instead of deionized water. The same procedure was followed when the solvents butoxyethanol and DEGME was tested with 2 wt% of solvent in combination with the polymers.

3. Results

The results of the test of the KHI PVCap and PNIPMAM with different additives at 0.1 to 0.5 wt% is shown in table 4. PVCap and PNIPMAM was first tested in deionized water at pH 7, and tested with the addition of 3 drops HCl at pH 1.

Table 4. Effect of Tcl/Tdp on PVCap and PNIPMAM with additives at 0.1-0.5 wt.% in DI water.

Additive	Concn. Wt. %	PVCap		PNIPMAM	
		0.25 wt. %	0.5 wt. %	0.25 wt. %	0.5 wt. %
Ca. pH 7, no adjustment			35/39		33/36
pH 1			36/42		35/39
3.5 wt.% NaCl			29/38		30/32
Non-ionics					
PVP 15k Mw=9000	0.5		33/39		32/35
PolyOx	0.5		33/44		32/37
PVFormamide	0.5		35/45		32/38
Poly(dimethylamine oxide) ethylacrylate	0.5		32/50		30/34
Trimethylamine oxide	0.5	34/52	31/38	80/>90	46/52
	0.25			80>90	
	0,1			80>90	
Polysaccharide, e.g. HEC	0.5		35/41		30/35
PEG Mw 1000	0.5		35/40		31/36
TEPA-Bu-AO	0.5		34/42		30/35
Polyglycerol 3	0.5		35/46		31/35
Cationics					
PVAmine 1595 (low Mw)	0.1	33/>90	34/48		
	0.15		35/71		
	0.25		35/>90		
	0.5		35/>90	35/40	34/39
PVAmine 9095 (high Mw)	0.1		33/42		
	0.25		33/46		
	0.35		35/68		
	0.5		33/>90	34/42	32/39
PolyDADMAC	0.1	34/66	35/45		
	0.25	34/56	35/48		
	0.35		33/70		
	0.5	35/>90	35/>90		32/39
HPEI Mw1800	0.5		34/46		32/38
HPEI Mw18000:HCl 2:1	0.25	32/65			
	0.5		32/80		
HPEI Mw18000:HCl 1:1	0.5		33/56		29/34
LPEI Mw2500 pH 3-4	0.1		31/57		
	0.25	33/>90	31/68		

	0.5		32/>90	31/38	31/35
LPWI Mw25000 pH 3-4	0.25	32/64			
	0.5		31/60		29/35
Poly(3-acrylamidopropyl) trimethylammonium chloride	0.5		33/60		29/35
PolyDMAPMA	0.25		35/47		31/34
	0.5		35/64		
PolyMAPTAC	0.5	35/73	35/72	32/38	31/36
PolyMADAME	0.5		34/38		32/36
Polyhexanide	0.5		32/52		32/38
Polylysine.HCl	0.5		32/38		45/52
1,4-diaminobutane.2HCl	0.5		30/47		
Bu6GuanCl	0.5	35/53	34/50		32/36
Anionics					
Polyacrylate Sokalan PA20	0.5		32/50		35/50
PVS Mw 3000 pH 4	0.5		32/54		33/40
	0.25		41/50		31/39
Polyaspartate B-3D	0.5		33/37		35/45
Lignosulfonate	0.5		>90/-		31/35
	0.25	>90/-			
	0.15		50/>90		
	0.05		41/50		
Solvents					
PVAmine 1595, 1 wt% 2-Butoxyethanol	0.5				31/36
	0.15		34/50		
PolyDADMAC, 1 wt% 2-Butoxyethanol	0.25	35/48			
PolyMAPTAC, 1 wt% 2-Butoxyethanol	0.5				28/34
PVAmine 1595, 1 wt% DEGME	0.5				31/35
	0,15		35/>90		
PolyDADMAC, 1 wt% DEGME	0.25	35/51			
PolyMAPTAC, 1 wt% DEGME					29/33

The KHI PVCap was also tested in 3.5 wt% NaCl solution in combination with other polymer, the results of these test are shown in table 5.

Table 5. Effect of Tcl/Tdp on PVCap and PNIPMAM with the best additives at 0.1-0.5 wt% in 3.5 wt% NaCl.

Polymer	Concentration ppm	PVCap		PNIPMAM	
		2500ppm	5000ppm	2500ppm	5000ppm
No 2 nd polymer			29/38		30/32
Cationics					
PVAmine 1595 (low Mw)	0.25	28/>92	29/44		
	0.5		29/64		
PVAmine 9095 (high Mw)	0.5		29/70		
PolyDADMAC	0.25	28/68			
HPEI Mw1800:HCl 2:1	0.25	28/46			

The results of testing trimethylamine oxide in combination with polymers is shown in table 6.

Table 6. The effect of trimethylamine oxide with different polymers

			Trimethylamine oxide	
			In H2O	0.25 wt.%
poly(N-isopropylacrylamide)	0.25		32/38	35/55
Polyacryloylpyrrolidine	0.25		45/50	55/>90
Poly(N,N-diethylacrylamide)	0.25		30/34	30/34
PolyNvinylisobutyramide	0.25		33/36	33/37

The effect of adding PVAmine 1595 to 0.5 wt % PVCap is shown in figure 11. The elevation of the deposition temperature of PVCap is clear with increasing concentration of PVAmine. It should be noted that the deposition temperature of PVCap with 0.25 wt% and 0.5 wt% PVAmine is above 90 °C.

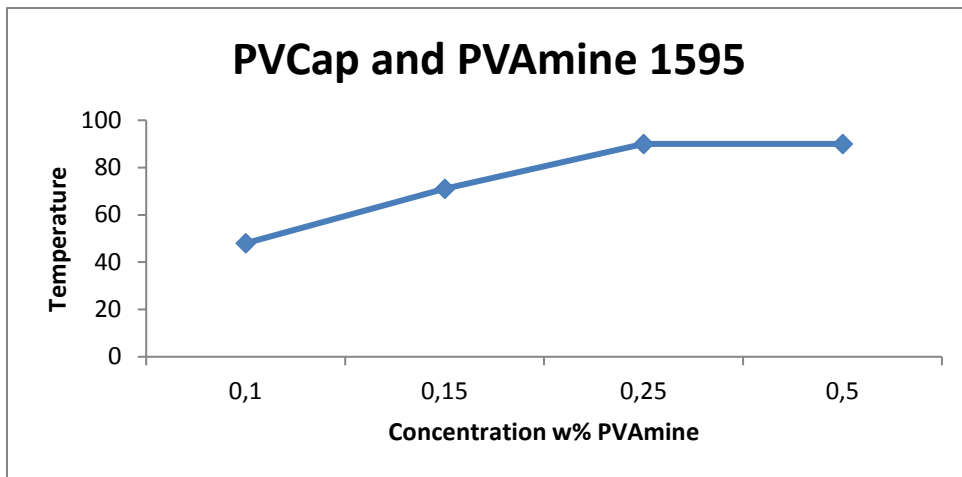


Figure 11. The deposition temperature of PVCap with increasing concentration of PVAmine 1595.

The addition of 0.1-0.5 wt% polyDADMAC to 0.5 wt% PVCap is shown in figure 12. The figure shows the increase of the deposition points of PVCap with increasing concentration of polyDADMAC. At the concentration of 0.5 wt% polyDADMAC, the deposition point of PVCap is $>90^{\circ}\text{C}$.

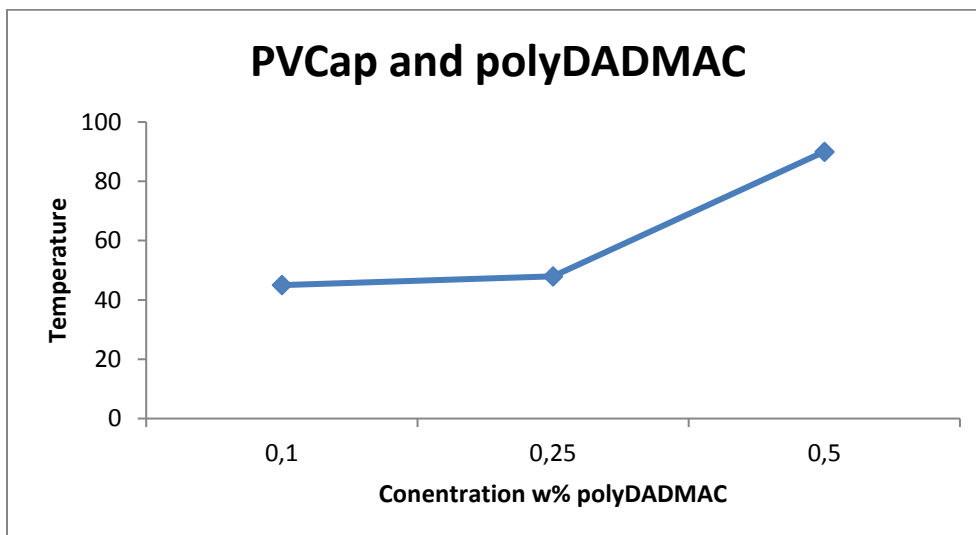


Figure 12. The deposition temperature of PVCap with increasing concentration of polyDADMAC.

The effect on the deposition temperature of 0.5 wt% PVCap with 0.1-0.5 wt% PVAmine 9095 is shown in figure 13. The graph shows increasing deposition points with increasing concentration of PVAmine. The deposition temperature at 0.5 wt% PVAmine is $>90^{\circ}\text{C}$.

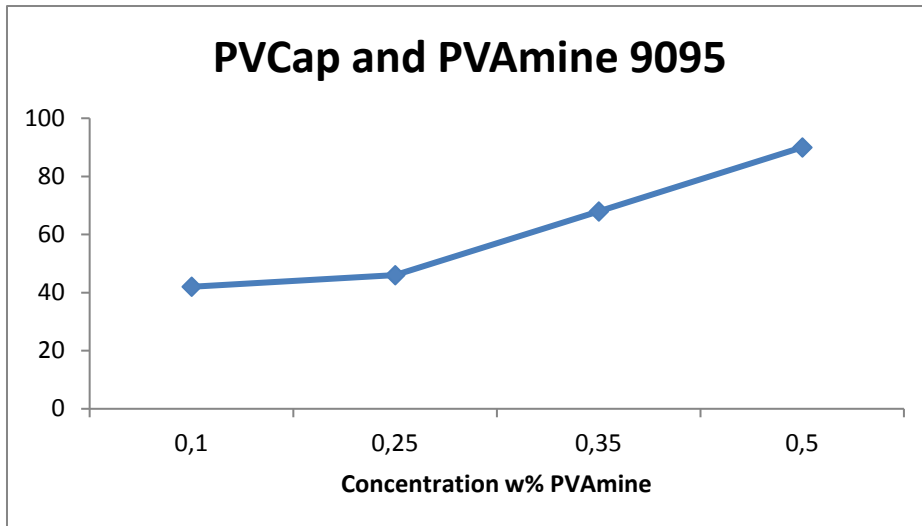


Figure 13. The deposition temperature of PVCap with increasing concentration of PVAmine 9095.

The effect of the LPEI with M_w 2500 on the deposition temperature of 0.5 wt% PVCap is shown in figure 14. The deposition temperature with 0.5 wt% LPEI is >90 °C.

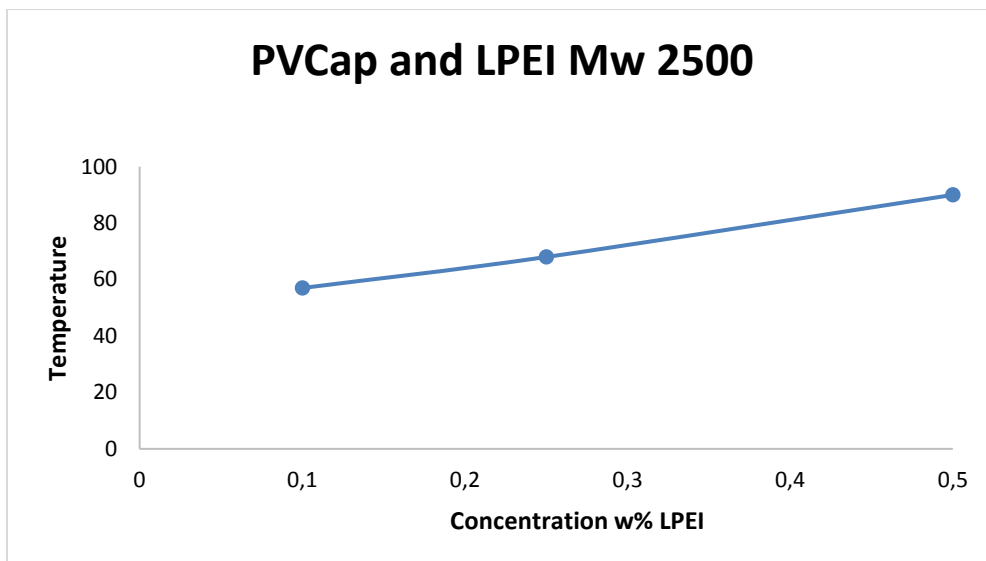


Figure 14. The deposition temperature of PVCap with increasing concentration of LPEI $M_w=2500$

To determine if the best Tdp enhancers would affect the KHI performance of the polymers, PVCap and PNIPMAM, a few KHI tests were carried out by PhD stipend Qian Zhang. The PVCap tests in table 7 were carried out in sapphire rocking cells as we had an ongoing project already in progress and we had baseline data for PVCap alone already. The cells have volume 20ml. They were filled with 10ml of aqueous solution (DI water + additives) and pressurized

to 76 bar with a structure II-forming gas mixture. were rocked at 20 rocks and cooled from 20.5°C to 2°C at 1°C/h. The test procedure has been reported before [41]. Basically, the lower the onset temperature (To) the better the performance.

Table 7. Constant cooling KHI performance screening tests in sapphire rocking cells. Average of 6 tests.

Polymer (2500ppm)	T _{dp} enhancer	To / °C	Ta / °C
No additive		16.0	
PVCap		11.2	10.4
PVCap	PVAmine.HCl low Mw, 2500ppm	11.0	10.0
PVCap	Polyhydrazide, 2500ppm	11.3	8.7
PVCap	Sodium lignosulfonate, 2500ppm	12.9	12.6
PVCap	Sodium lignosulfonate, 750ppm	11.2	10.8

In addition, we also looked at PNIPMAM mixed with TMAO. We also had an ongoing project in steel rocking cells so we used this equipment for these tests. The test method and conditions were the same as with the sapphire rocking cells, except the steel cells have volume 20ml and we filled them half way with test solution. The results are given in table 8.

Table 8. Constant cooling KHI performance screening tests in sapphire rocking cells. Average of 5 tests.

Polymer (2500ppm)	T _{dp} enhancer	To / °C	Ta / °C
No additive		16.0	
PNIPMAM		9.4	9.1
PNIMPAM	TMAO 2500pm	10.5	10.1

41. Chua, P.C. and M.A. Kelland, *Poly(N-vinyl azacyclooctanone): A More Powerful Structure II Kinetic Hydrate Inhibitor than Poly(N-vinyl caprolactam)*. Energy & Fuels, 2012. **26**(7): p. 4481-4485.

4. Discussion

This work has mainly focused on the effect of different methods to raise the deposition point of a known KHI by addition of other polymers or additives to the KHI. There are several methods that has been discussed in this paper; the use of denaturing agents, surfactants or by copolymerization. The effect of denaturing agents on protein folding and stabilization of polymers could have a major effect on the cloud point and deposition point of polymers due to their interaction to stabilize the polymer when the temperature is increased, but there is a concern to the performance of the KHI when denaturant agents are used with a KHI. Reference [32] in chapter 1.5.2 suggests that the effect of TMAO to counteract denaturing may be due to the ability of the amine oxide to hydrogen-bond with $-NH-$ groups in proteins. Table 6 shows that the T_{cl} and T_{dp} of PNIPMAM was raised by TMAO which fits this theory as $-NH-$ groups are available in the side chains. The T_{cl} and T_{dp} of PNIPMAM was $33^{\circ}C$ and $36^{\circ}C$ respectively in deionized water. When TMAO was added, the T_{cl} was raised to $80^{\circ}C$ and T_{dp} was raised to above $90^{\circ}C$ at concentration of 0.25 wt% of PNIPMAM with concentration of 0.1-0.5 wt% TMAO. PVCap did not have the T_{cl} and T_{dp} significantly raised by TMAO which also fits the theory as PVCap has no $-NH-$ groups. Therefore, we needed to test if other polymers with $-NH-$ groups also have their T_{cl} and T_{dp} raised by TMAO, we chose to test polyvinylisobutyramide. Also, as a proof of the opposite effect, we needed to show if the T_{cl} and T_{dp} of other polymers without $-NH-$ groups were not affected by TMAO. We chose polyacryloylpyrrolidine and poly-N,N-diethylacrylamide. The effect of TMAO on the T_{cl} and T_{dp} of polyacryloylpyrrolidine shows an increase which is the opposite of what was expected, as shown in table 6. This shows that this does not always fit the theory.

TMAO was the only non-ionic that effected the T_{dp} of a KHI. The other non-ionic polymers did not have any major effect on T_{cl} and T_{dp} for both PVCap and PNIPMAM. This is perhaps explained by that there is no interaction between the neutral polymers and KHIs. The greatest effect on T_{dp} for PVCap was observed with the addition of cationic polymers such as PVAmine. The low M_w PVAmine 1595 had greater effect on T_{dp} than the high M_w PVAmine 9095. The T_{cl} and T_{dp} of PVCap in deionized water was $35^{\circ}C$ and $39^{\circ}C$ respectively. With the addition of PVAmine 1595 the T_{cl} was still the same at $35^{\circ}C$, but the T_{dp} was raised to above $90^{\circ}C$ when the concentration was above 0.25 wt%. As shown in figure 11, with increasing concentration of PVAmine 1595 the T_{dp} of PVCap increases but the T_{cl} stays the same. Figure 13 shows the effect of PVAmine 9095 with increasing T_{dp} of PVCap with increasing concentration of PVAmine 9095. The difference in the length of these cationic polymers shows that the low M_w polymers can perhaps interact with more molecules when the KHI is reaching the folded state and keep the polymer more hydrated by hydrogen bonding. When the temperature is increased, the balance of the hydrophobic and hydrophilic interactions is then altered, and the addition of a cationic polymer can increase the deposition temperature by either interacting with the polymer directly or by interacting with the surrounding water molecules making the polymer more hydrated. The effect of another cationic polymer, the polyDADMAC, shows to have great effect on the T_{dp} of PVCap.

Figure 12 shows the effect of adding 0.1-0.5 wt% of polyDADMAC to 0.5 wt% PVCap. The increase of concentration of polyDADMAC gives increasing T_{dp} . The position of the cation is maybe also important factor to be considered. We can assume that the closer the cation is positioned to the backbone of that polymer the better effect it can have on the T_{dp} of the KHI. The use of both hyper branched polyethyleneimine (HPEI) and linear Polyethyleneimine (LPEI) can support that theory. The results show that the LPEI had greater effect on T_{dp} than that of HPEI. The T_{dp} was above 90 °C for 0.25 wt% PVCap and 0.25 wt% LPEI Mw 2500, compared with T_{dp} of 65 °C when 0.25 wt% HPEI was added. Figure 14 shows the increase of T_{dp} of PVCap with increasing concentrations of LPEI. The LPEI and HPEI was protonated by adding HCl that gave these cationic polymers in low pH. There were also tests done to see the effect of pH on T_{cl} and T_{dp} for PVCap and PNIPMAM. The addition of three drops HCl gave pH 1 and the T_{cl} and T_{dp} was only raised to 42 °C for PVCap and 39 °C for PNIPMAM. This shows that the pH does not have a major effect on T_{cl} and T_{dp} . The effect of NaCl on the T_{cl} and T_{dp} with the KHIs of PVCap and PNIPMAM was also investigated. The T_{cl} and T_{dp} of PVCap was lowered as expected to 29 °C and 38 °C respectively, and T_{cl} of 30 °C and T_{dp} of 32 °C for PNIPMAM. Table 5 shows the effect of using a 3.5 wt% NaCl solution when testing the T_{cl} and T_{dp} when adding a cationic polymer to PVCap. The results show that salt can impact the T_{dp} when adding PVAmine 1595 and PVAmine 9095 with concentrations of 0.5 wt%. The T_{dp} was lowered by approximately 20 °C, and that was to be expected. This can be related to the Hoffmeister effect with the addition of salts by the effect of anions and cations on polymers.

There are also several cationic polymers that was tested that did not have any effect on T_{dp} such as polyMADAME, polyDAPMA and Polylysine.HCl. With both PVCap and PNIPMAM the T_{cl} and T_{dp} stayed the same when adding these polymers. The reason could be that the cation in their structure is positioned to far from the backbone of the polymer and making any interaction too difficult with the KHI. In the case of anionic polymers, the effect on T_{cl} and T_{dp} did not have as great impact as the cationic polymers, but the only exception being the lignosulfonate with PVCap. The addition of 0.5 wt% of lignosulfonate to 0.5 wt% PVCap had T_{cl} above 90 °C, showing a clear solution at high temperatures. It is possible that there has been a reaction between lignosulfonate and PVCap that caused the increase of T_{cl} and no deposition at high temperatures. When the other anionic polymer polyacrylate and PVS was added to PVCap, the T_{dp} was raised to 50 and 54 °C respectively. With PNIPMAM, the addition of polyacrylate raised the T_{cl} to 50 °C. The reason for the difference between the effect of cationic polymers having stronger effect than the anionic polymers is unknown. One possible explanation could be that the same effect of the Hoffmeister series were the anions show to lower the T_{cl} in some cases while the cations show to not have that great effect. The effect of adding salts that are anionic and cationic are explained in section 1.5.1. The addition of anions could in some cases lower the cloud point of polymers, but when there is a polymer with anionic or cationic side groups, the effect on the T_{cl} and T_{dp} is different. Whereas a single molecule that is ionic have a capability of lowering T_{cl} and possibly T_{dp} of a polymer, the addition of ionic polymers will interact in a different way causing the opposite effect and possibly increase T_{cl} and T_{dp} . The reason could be that the hydrophobic and hydrophilic interactions is greater when a polymer is added compared with the interaction of single ionic molecules that interrupts the hydrophilic interactions with the surrounding water molecules.

It is common to use solvents to dissolve the KHI before they are used in the field. The KHI usually are too viscous and need to be dissolved in a blend of several solvents before they are injected. The effect of a solvent on T_{cl} and T_{dp} could be a factor to be considered. Several tests with the solvent of butoxyethanol and DEGME were done to see if there is any impact of the solvent on the T_{cl} and T_{dp} of the KHI. When adding 1 wt% butoxyethanol to a solution with 0.15 wt% PVAmine and 0.5 wt% PVCap, the T_{dp} is lowered to 50°C compared to a solution without the solvent with T_{dp} of 71°C. This shows that in some cases that the solvent could interfere with the effect of the cationic polymer that is added. But when 1 wt% of the solvent DEGME was added, the T_{dp} was raised to above 90°C. This shows that the choice of solvent could have a major impact when considering the T_{dp} of a KHI of PVCap. The effect of the solvents was not significant when they were used with PNIPMAM as shown in table 4. The T_{cl} and T_{dp} stayed almost the same when butoxyethanol and DEGME were used.

The results from the performance tests on PVCap show that the cationic polymers PVAmine.HCl with low Mw and the polyhydrazide do not significantly affect the KHI performance. The sodium lignosulfonate at 2500ppm did affect the T_o value negatively at 2500ppm, but not at 750ppm. At 750ppm we still get good increase in T_{dp} value for the PVCap. The results for performance in table 8 show that the TMAO has a small negative effect on the average T_o value.

5. Conclusions

The tests showed very rarely any significant effect on T_{cl} at these concentrations, but some additives have significant effect on T_{dp} . The use of additives with a KHI shows that it is possible to increase the T_{dp} of a KHI, thus making the polymer soluble at higher temperature. Even if the polymer still gets cloudy at low temperatures, the main target was to keep the KHI soluble and not deposit at high temperatures. The pH does not have a big impact on T_{dp} of the KHIs. Most non-ionic polymers did not show any significant effect on T_{dp} for both PVCap and PNIPMAM, with exception of TMAO. The non-ionic TMAO gave significant increase on T_{dp} only with PNIPMAM. The cationic polymers were in general the best additives, were the low M_w polymers showed the most impact on the T_{dp} of PVCap. The best cationic polymer that showed the greatest effect was PVAmine 1595. It is possibly because the charge is close to the backbone of that polymer. This polymer works well with PVCap but not for PNIPMAM. Even though both PVCap and PNIPMAM are amide-based non-ionic polymers, the effect of certain polymers has great impact on T_{dp} for PVCap but not any effect for PNIPMAM. The reason for that is still unknown and further research on the effect of additives with PNIPMAM is needed. Only one anionic polymer showed to have significant effect on T_{dp} with PVCap, the sodium lignosulfonate showed to increase T_{cl} and T_{dp} at low concentrations. This surprising good effect of sodium lignosulfonate could be related to the aromatic ring in the lignosulfonate structure. The performance tests show that TMAO had little effect on the KHI performance of PNIPMAM, and the sodium lignosulfonate had also little effect on the performance of PVCap. This shows that it is possible to keep the KHI polymers soluble at high temperatures without losing KHI performance.