Gas Hydrate Formation and Control by the Use of Chemicals

Master Thesis

by

Chittawan Nakarit

University of Stavanger

Faculty of Science and Technology
Department of Mathematics and Natural Science

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ABSTRACT

Gas hydrates formation and plugging of pipelines is becoming an even more serious problem in the oil and gas industry due to the exploration and development moving to more extreme locations. Kinetic hydrate inhibitors (KHIs) are one class of low dosage hydrate inhibitors (LDHIs) which are used to prevent hydrate plug in pipelines. They work by delaying gas hydrate formation by time periods dependent mainly on the subcooling (driving force) in the system.

The effect of various parameters on different kinetic hydrate inhibitors (KHIs) has been examined with high pressure rocking cell equipment (RC5 unit) in this thesis. Since no one has published a study to compare KHI performance between rocking rigs and autoclaves this has been investigated in this study. Constant slow cooling experiments were conducted until hydrate formation started (T_o value) and hydrate plug formation (T_a value) occurred. All the different apparatuses gave similar performance trends with high performance KHIs, but T_o was different with low performance chemicals. This may be due to the stochasticity of gas hydrate formation. The reproducibility of T_o and T_a values from RC5 are as good as both autoclaves.

The RC5 experiment at constant cooling showed that the KHI efficiency increased when concentration dose was increased from 2500 ppm to 5000 ppm. For all the experiments, the present of small amounts NaCl in aqueous solution decreased the onset and catastrophic hydrate formation temperature by 0.1-2.1^{o}C compared with using DI water alone. This is beyond the thermodynamic hydrate inhibition effect of the salt and shows varying degrees of synergy with added salt. For ranking inhibitors at dosed 2500 ppm, the test results indicated the best chemicals is Inhibex Bio800 followed by Inhibex 101, Hybrane, PVCap 12k+TBAB, and Inhibex 501. Whereas at dosage of 5000 ppm, Inhibex Bio-800 inhibited hydrate formation as well as Inhibex 101.

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Chittawan Nakarit

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1 INTRODUCTION

The formation of water and gas molecules into a solid phase known as clathrates are called gas hydrates [1]. Gas hydrates are one of the serious economic and safety problems in petroleum industry during the exploration, production, processing and transportation of natural gas and liquid [2]. Pipelines and processing equipment can be blocked by their formation [3]. These blockages reduce and stop flow potential that means production loss or operation shut down. Formation of gas hydrates can take place during operation and shut in periods [4]. It can be very difficult and costly to remove them [5].

Normally appearance of gas hydrates are under high pressure (>30 bar) and low temperature (<20^{o}C) condition. The fluid compositions also affect its formation [6]. These are regular situations for seabed or cold climate wet gas or multiphase flow lines (oil/water/gas) [4]. Nowadays, exploration and production of petroleum are moving to more extreme conditions. Hence, the problem of gas hydrates formation is more challenging [7]. Numerous approaches have been developed to protect against gas hydrate plugging. The four preventative methods of gas hydrates plugging in industry are removing the water (dehydration), heating the gas to temperature above the hydrate equilibrium at the operating pressure, keeping pressure below the hydrate equilibrium at the operating temperature, and using chemicals [8].

Although all of these procedures theoretically prevent hydrate formation, some of them are not suitable for the field. For example, dehydration may not be desirable for offshore operation because of space limitation for process equipment, therefore operators usually rely on chemical inhibitors [9]. Within the method of chemical control, thermodynamic inhibitors (THIs) are the most popular. THIs work by shifting the hydrate equilibrium curve to lower temperature and higher pressure condition [10]. However, these inhibitors are not only economical at high water cuts but also pose many environmental and logistical issues [11]. A Recent chemical method is usage of low dosage hydrate inhibitors (LDHIs) which have been utilized in the last two decades to accommodate the economical and HSE concerns. LDHIs are sub-divided into kinetic hydrate inhibitors (KHIs) and anti-agglomerates (AAs) [12-14]. Both of them do not change the thermodynamic condition of hydrate formation, but they limit or delay nucleation and growth [7]. In order to test LDHIs

performance, different testing equipment have been verified such as miniloop, large loop, autoclave and rocking rig [15].

In the present study, the performance of KHIs is evaluated in rocking cells. The objectives are verification and validation of results from a new rocker rig instrument by comparing with the old one that is already available in UIS. Effect and efficiency of several KHIs studies are also included. Furthermore, many studies have focused on new inhibitors and have demonstrated enhanced performance in the autoclave and rocking cell tests. However no studies have compared the performance of inhibitors between these two apparatuses. Thereby one of the purposes in this thesis is comparison of the results with 2 sizes of autoclave equipment under the same conditions of KHI concentration, SNG gas, pressure, and temperature. This study will be useful for further education or industry.

2 LITERATURE REVIEW

2.1 Gas hydrates definition and discovery

Gas hydrates are solid ice-like crystalline structures which consist of natural gas molecules are entrapped within cavities of water molecules. The crystalline compounds typically form at low temperature and high pressure conditions [4, 8].

In 1810, Sir Humphrey Davy discovered hydrates. It became an important issue in natural gas industry five decades later [16]. In 1934, Hammersmidt found that a hydrate blocked a flowline of oil and gas during transportation and production, like the one presented in Figure 2.1. Hydrates are not only a danger to oil and gas production installations, but they are also harmful to the people who work with them [17]. Since hydrates can plug the pipe, the pressure in pipe can be separated into two sections. The first part is upstream part that has high pressure and the other is downstream area which has low pressure. This different pressure can cause a rupture in the pipe segment by causing a plug solid projectile which is very dangerous and can lead to loss of human lives [18]. Therefore hydrate prevention and elimination methods with various approaches have been investigated and developed.

Figure 2.1 Formation of gas hydrate plugged in a subsea pipeline. Picture from Petrobras (Brazil) [19].

2.2 Gas hydrates structure

Hydrates are formed by hydrogen bond among water molecules. Results of these compounds molecule align to stabilize and precipitate into solid mixture [3]. Formation of gas hydrates cause by contacting of small guest molecule (< 0.9 nm.) such as methane or carbon dioxide with host under optimum temperature and pressure [1]. The host and guest molecules are defined as water molecules and the other compounds those stabilize the crystal [3]. Individual small guest molecule is entrapped in a cage of water molecules that has hydrogen bond between them as shown in Figure 2.2 and 2.3 [4, 8, 19]. A guest molecule is free to rotate within the cavity of water molecules because they have no bonding between host and guest molecule [3].

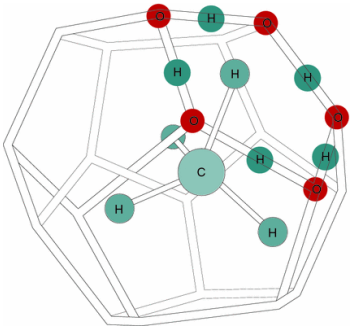


Figure 2.2 Molecular structures of gas hydrate [19].

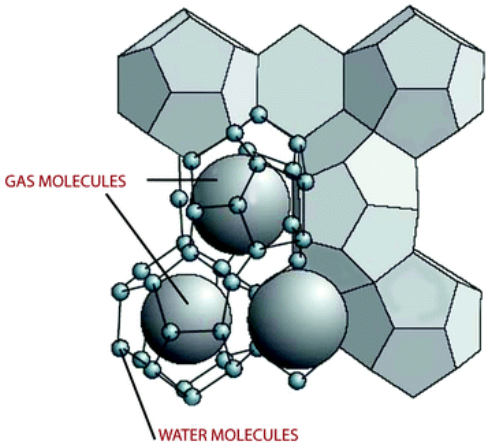


Figure 2.3 The inclusion of gas molecules in the gas hydrate lattice. The molecular-sized "cages" are composed of hydrogen-bonded water molecules (reproduced from SETARAM) [19].

Gas hydrates can form in three different crystalline structures depending on the composition of natural gas implicated during forming [8, 20]. These three structures are discussed in sections 2.2.1-2.2.3 below.

2.2.1 Structure I

Structure I (SI), Type I, and cubic structure I (CSI) are the same structure. SI holds small guest molecules (0.4-0.55 nm.) [1] or gases smaller than propane [21]. SI predominates in natural environments [1]. Figure 2.4a illustrated SI that is 6 large $5^{12}6^4$ water cages and 2 small 5^{12} water cages per unit cell. (A^n can be interpreted as, A is the face sides number of a cage and n is the number of faces in the cage holding) [14].

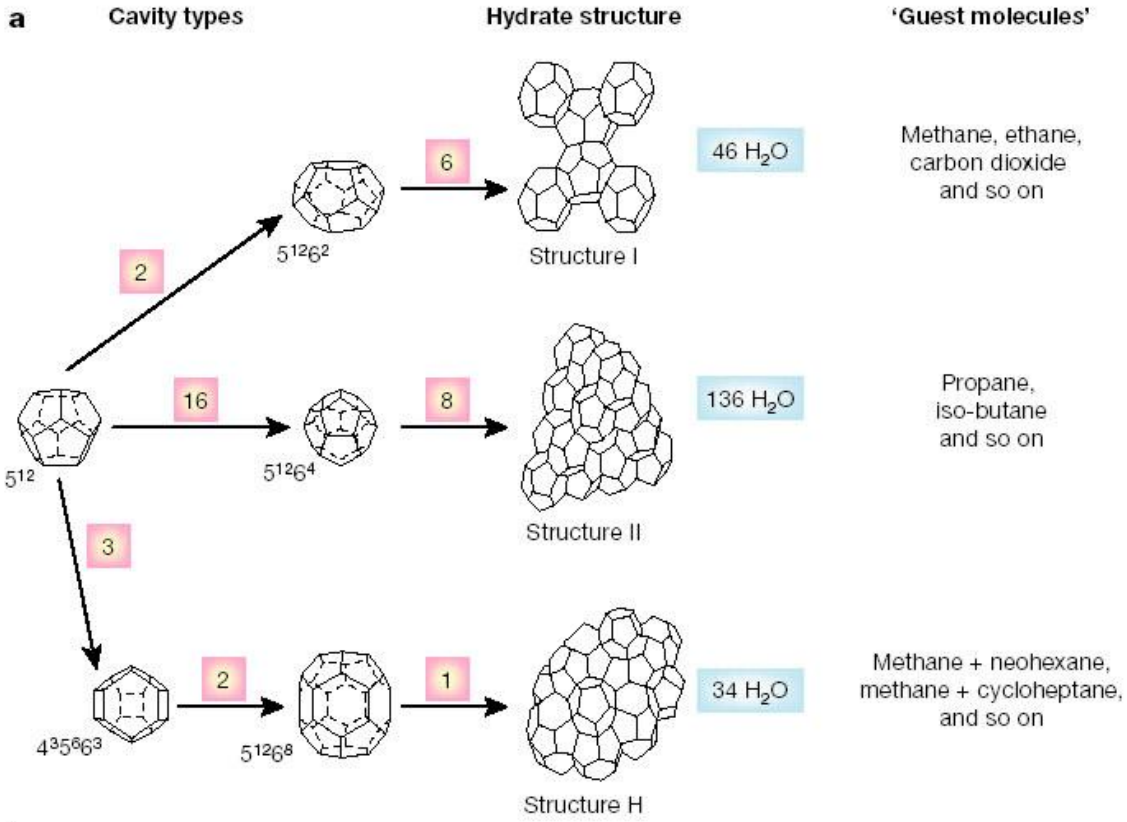
2.2.2 Structure II

Structure II (SII) is sometimes called a Type II or cubic structure II (CSII). SII contains gas guest molecule which are larger than SI (0.6-0.7 nm.) [1]. SII typically occurs with a few percent of molecules larger than ethane [13, 21]. This kind of structure is the most plentiful structure in the oil field environment that has 8 large $5^{12}6^8$ water cages and 16 small units of 5^{12} water cages per unit cell [14]. This is probably because larger hydrocarbons are present such as pentane and can fill in larger $5^{12}6^8$ cages, whereas smaller hydrocarbons for example CO_2 and H_2S can fill in smaller 5^{12} cages [22]. Molecules which are less than ~0.35 nm. in size are too small to stabilize into any cavities, while molecules size that are larger than 0.75 nm. are too large to fill within any cages to form structure I and II [13]. The other smallest gas molecules such as Ar, Kr, O_2 and N_2 those have diameter lower than 0.44 nm. form SII as well. The guest molecule size with SI and SII are shown in Figure 2.4b [1].

2.2.3 Structure H

Structure H (SH), Type H, or Hexagonal structure H (HSIII) is more complex than SI and SII [3]. In the oil and gas industry, this structure it is rarely found [4]. They form only when gas (guest molecules) are consisting of both small and large in sizes (0.8-0.9 nm.) [1].

All of three structures commonly contain only one non-polar guest molecule within each cage. A size of guest molecule has to be big enough to stabilize in cavity, but not too big to fill the cavity [13]. However, under unusual conditions such as at very high pressure they can have multiple cage occupancy with unusually small guest molecules e.g. hydrogen and noble gasses [1, 23].



b

Hydrate crystal structure	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91†	4.06†	5.71†
Coordination number*	20	24	20	28	20	20	36
Number of waters per unit cell	46		136		34		

*Number of oxygens at the periphery of each cavity.
†Estimates of structure H cavities from geometric models.

Figure 2.4 The three hydrate crystal structure [1].

2.3 Hydrate formation and dissociation process

Hydrate nucleation and growth may have the same process as crystallization process such as precipitation of salt from solution. Gas hydrate formation is a time dependent process that can be divided into hydrate nucleation, hydrate growth and dissociation as illustrated in Figure 2.5 [8].

2.3.1 Hydrate nucleation

Hydrate nucleation is the process that produces a small labile cluster. It is called a hydrate nuclei. This cluster consists of water and gas molecules. It grows, disperses and tries to grow further because a labile cluster is unstable and ready for continuous changing [8]. The general hydrate gas formation formula is expressed by equation below.

$$M\ (g) + nH_2O\ (l) \leftrightarrow M{\bullet}nH_2O\ (s) \qquad (1)$$

Where M is natural gas molecules, n is number of water molecules required to form a gas hydrate per one molecule of gas, and $M{\bullet}nH_2O$ is gas hydrate [7, 16].

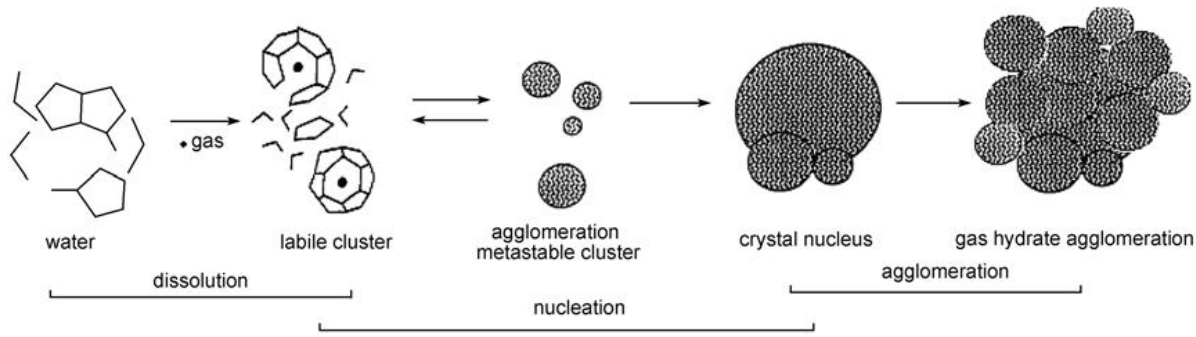


Figure 2.5 Hydrate formation hypothesis [7, 13].

2.3.2 Hydrate growth

After the hydrate crystal nucleation step, the crystal growth process occurs continuity to agglomerate gas hydrate as in Figure 2.5. The combination of three parameters should be considered. These are the kinetics of crystal growth at the surface of hydrate, mass transfer components to the growing surface, and heat transfer away from the growing surface. The

major factors are mass and heat transfer of growth process as illustrated in Figure 2.6. They carry out at constant volume and temperature changes during an experiment. From point 1, that gas reacts with water after that the pressure is reducing linearly with temperature. There is no hydrate formation during 1 and 2 period which is defined as induction time (nucleation time, induction period or lag time) because of metastability [8, 13]. Induction time is time taken from entering to hydrate forming region and the onset of hydrate formation [9]. Point 2 is the beginning of hydrate formation. After that pressure dramatically falls to point 3, the result in rapid hydrate growth through the end of growth for hydrate formation at point 3. After the system is heated, hydrate dissociation start from point 3 to A. Hence, the pressure slightly increases at the beginning and then sharply rises until point A. This point is called the hydrate equilibrium temperature and pressure [8]. However, the information for the crystal growth rate after nucleation still has limited.

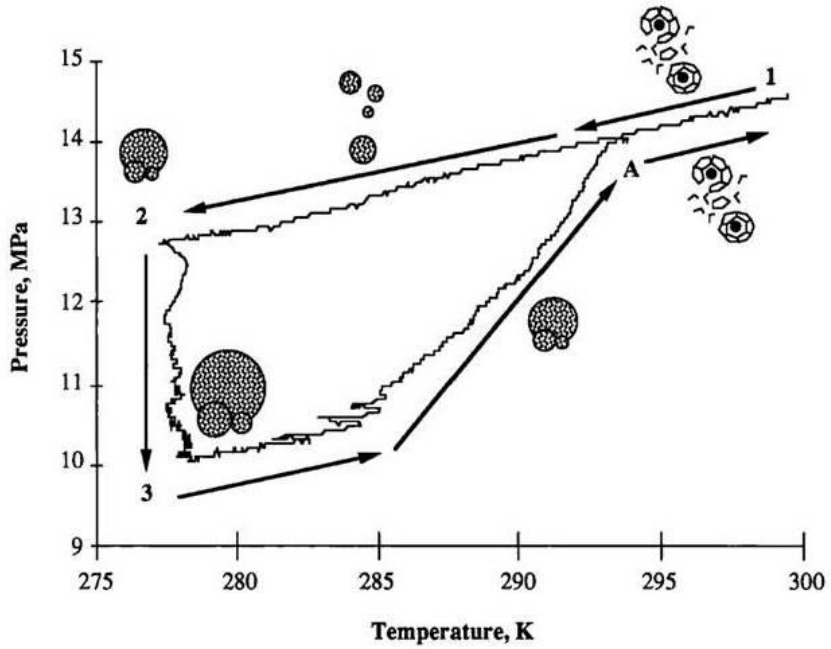


Figure 2.6 Diagram of temperature and pressure trace for methane hydrate formation [13].

2.3.3 Hydrate dissociation

Hydrate dissociation is an endothermic and vital process to eliminate hydrate crystal which blocks pipelines in oil and gas industry. Thus decomposition of gas hydrate to water and gas molecules can be success by supply external heat to destroy hydrogen bond between water molecule and van der Waals interaction between host and guest molecule [8]. There are

different approaches which can be applied to mitigation a plug of gas hydrate such as dehydration, heat management, and chemical inhibition [8, 24].

All of three methods have been used in the field. Among these methods, chemical inhibition is the most common to prevent and reduce gas hydrate formation [25].

2.4 Chemical inhibition and hydrate removal

Chemical inhibitors are generally classified to two different forms for preventing hydrate blockage in pipeline. These two classes are as follow [4].

2.4.1 Thermodynamic hydrate inhibitors (THIs)

THIs or hydrate antifreezes are the most common chemicals used for hydrate inhibition. They act by modifying the bulk thermodynamic properties of the fluid system. Hence, the equilibrium condition for a gas hydrate formation temperature and pressure becomes lower and higher, respectively [4] as depicted in Figure 2.7. If the application of THIs are enough in concentration, hydrate will no further form at the operating temperature and pressure [12].

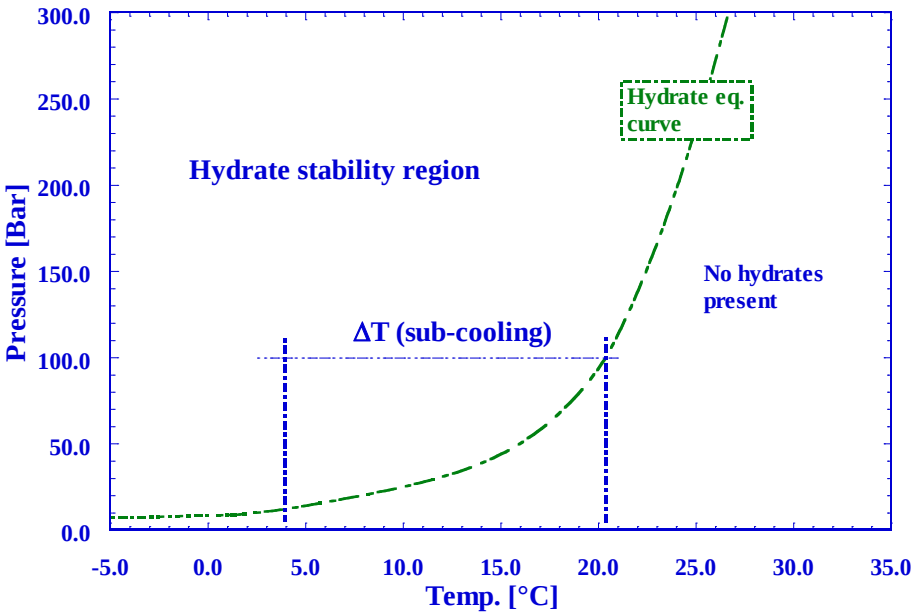


Figure 2.7 Pressure-temperature diagram for a typical natural gas hydrates [4].

Alcohols, glycols, and salts are well known chemicals, used for thermodynamic hydrate inhibition for example methanol (CH_3OH) and monoethylene glycol (MEG, $HOCH_2CH_2OH$) are widespread used in production, workover, process operation, and for melting hydrate plugs. Diethylene glycol (DEG) and triethylene glycol (TEG) are rarely used for hydrate prevention because of lower efficiency [4] but TEG is the most popular for dehydration processes [3].

The industry uses the Hammerschmidt equation to estimate the hydrate depression temperature for THIs in the aqueous liquid as shown in the equation below.

$$\Delta T = \frac{KX}{100M - MX} \quad (2)$$

Where ΔT is subcooling, ^{o}F

K is constant, depending on the type of solution

X is the required concentration of an inhibitor in an aqueous solution

M is the inhibitor's molecular weight

K values and molecular weights of inhibitors are given in Table 2.1 [26].

Table 2.1 Physical constants of inhibitors.

Component	Molecular weight	K-value
Methanol	32	2335
Ethylene Glycol	62.07	2700
Diethylene Glycol (DEG)	106.12	4000
Triethylene Glycol (TEG)	150.17	5400

From the equation, the key parameter for inhibition performance is molecular weight. For example, MeOH (methanol) has lower molecular weight than DEG so MeOH has better inhibitor performance than DEG.

Among the THIs, methanol is generally used once and not recovered but discharged into the environment. Glycol is a little more expensive and is therefore usually regenerated [3]. Although methanol and glycol are relatively cheap, these chemicals are used at high

concentrations in the water phase (10-60 wt.%) [27]. Thereby the recovery and reuse of THIs are usually considered. Another class of THIs are water-soluble salts, for example sodium chloride, calcium chloride, and potassium formate. They are used for hydrate prevention in drilling fluids. Some drilling applications use a combination of salt and glycols. Nevertheless, high concentration of salt in drilling fluid can increase the corrosion potential. Other THIs chemicals have been tested but they are currently not used in the field because of more expensive and lower inhibitor performance than methanol and MEG. Some examples of these chemicals are dimethylformamide, N-methyl pyrrolidone, ethanolamines and isopropanol [4].

However, there are various problems from these chemicals class e.g. corrosion, Health, Safety and Environment (HSE) and logistic concerns, high Capital Expenditure (CAPEX) and Operational Expenditure (OPEX) costs [3, 21, 28]. Due to the disadvantages of THIs, numerous researchers attempt to develop a new generation of chemicals. The Low Dosage Hydrate Inhibitors (LDHIs) are the new developed inhibitors. They are called LDHIs because they can be used in lower concentration than THIs. LDHIs are divided into two main classes: Kinetic inhibitor (KHIs) and Anti-agglomeration (AAs). The main differences between THIs and KHIs are the lower concentration needed for KHIs and the mechanism of hydrate inhibition [17].

2.4.2 Low Dosage Hydrate Inhibitors (LDHIs)

1) Kinetic inhibitor (KHIs)

KHIs are water soluble polymers. They usually consist of other small organic molecules which are added for efficiency enhancement (synergists). KHIs generally have small cyclic amide groups as the active units [4, 14, 29]. The purpose of KHIs is to delay gas hydrate nucleation and crystal growth. The induction time or delay time usually depends on the degree of subcooling (subcooling, ΔT, is the temperature difference between the hydrate dissociation temperature and the operating temperature at a given pressure, and is the driving force for the hydrate formation) [3, 4]. The commercial KHIs generally have maximum subcooling around 9-10^{o}C (16-18^{o}F). The main advantage of KHIs are low concentration usage (<1 wt.%) [4].

Due to lower consumption of KHIs compared to THIs, KHIs are becoming more and more widely used which will affect OPEX/CAPEX saving and extended in the field lifetime [21]. Moreover, KHIs are cleaner and safer than THIs for the environment. KHIs have both advantages and limitation. The drawback of KHIs is less than 13^{o}C subcooling application [17] and short shut-in period when compared to AAs [27, 30]. Common examples of KHIs are polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) [12, 31]. A copolymer of vinylmethylacetamide (VIMA) and vinylcaprolactam (VCAP), or poly (VIMA/VCAP) show more advantage of this copolymer than methanol and safer for discharging [9]. The comparison between PVP and GHI1 (composed of polyvinylpyrrolidone and diethylene glycol monobutylether in the weight ratio 1:1) was observed in 2010 by Tang CuiPing et.al. They found that GHI1 had stronger inhibition ability than PVP [7].

The effort has led to development to increase the inhibition performance by the combination of two approaches or various molecules. For instance, the mixture of KHIs and corrosion inhibitor (CI) are used in the North Sea [11]. The combination of THIs and KHIs gives better result [10]. For example, the new hybrid of KHIs and THIs can give longer induction time (8-12 days) and higher subcooling (17.7^{o}C) than THIs or KHIs alone [14, 28].

2) Anti-agglomeration (AAs)

AAs are one of the LDHI classes. The effective concentration is lower than 1 wt.% [17]. They work by preventing agglomeration of hydrate crystal into a large size. The formation of gas hydrate formation still occurs but the crystals do not plug and can be transported through the pipeline because the size of the gas hydrate crystals is small. However, they only work when a liquid hydrocarbon phase is present, i.e. crude oil or condensate. AAs are less independent of time and the degree of subcooling of the system compared to KHIs. They can be used in deepwater applications [4] but effecting in low water cut systems [29].

At present, combination of KHIs and AAs are alternatives for delaying hydrate formation and hydrate plug prevention respectively [17].

2.5 Test apparatuses for inhibitors

Gas hydrate inhibition performances of newly synthesized polymers have been verified by various procedures. These are roughly classified into 2 techniques, screening and real field fluid/gas flow simulation. Each of them has a specific apparatus. However, results cannot be compared [32]. These apparatuses are discussed in section 2.5.1-2.5.4 below.

2.5.1 Screening method

This method is simpler than simulating of real flow conditions. Performance testing is conducted by using a mixture of Tetrahydrofuran (THF) and water for wet gas simulation. Within the same temperature range, this mixture solution can form hydrate crystals as wet gas [32]. In the mixtures of THF and water, THF hydrate crystals occur at around 4.4^{o}C at atmospheric pressure. THF forms SII hydrate which is usually formed by natural gases from most oil or gas fields [33].

The hydrate crystal growth inhibitions of a single THF have been observed by mixing sodium chloride (NaCl), THF and distilled water. This solution produces an appropriate stoichiometric form of THF SII hydrate. In this solution, hydrate formed around 3.2^{o}C [33]. The tested additives are added in solution and kept in a beaker at the atmospheric pressure. After that, the beaker is immersed in a cooling bath. At thermal equilibrium, the ice crystals are introduced to THF hydrate formation and growth. Then, the weight and morphology of the crystal is measured and determined [32, 33].

2.5.2 High pressure autoclave

There are 2 types of autoclave used for hydrate inhibition performance tests: the sapphire cell equipment and stainless cell steel as shown in Figure 2.8 and 2.9 respectively [34]. Hydrate formation in autoclave is detected by three apparatuses. These are: 1. visual detection of hydrate crystals, 2. pressure decline in vessel owing to gas consumption, and 3. temperature increase (exothermal) since heat is released during the formation of hydrates. Nevertheless, exothermal detection of hydrate formation is not easy because of the high water mass used in autoclave [28].

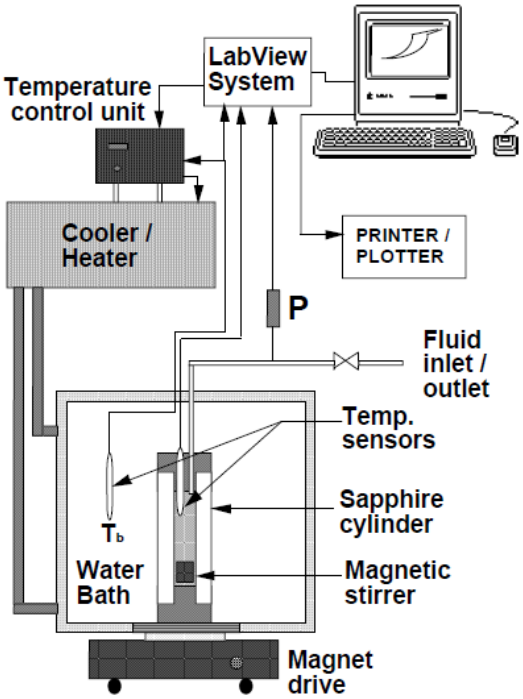


Figure 2.8 Sapphire cell high-pressure test apparatus [34].

Figure 2.8 illustrates the sapphire cell in a water bath. A sapphire tube is fitted between two stainless steel holders with end pieces. The sapphire cell is prepared with a stirrer mechanism. At the bottom, a stirrer blade is connected to the magnet housing via an axle. A magnet drive is used to create rotating magnetic field. Sometimes torque exerted on blade is measured [12]. Visual detection through transparent carbonate plastic cylinders can be seen by four separate windows at 0^o, 90^o, 180^o and 270^o. The temperature control unit connected with cooler/heater unit. Figure 2.9 shows the stainless steel autoclave which has all steel parts [34].

Figure 2.9 Top view of a stainless steel autoclave and screw-top [33].

2.5.3 Rocking cell

Rocking cell, rocker rig or the ball stop rig is one piece of the LDHIs testing equipment. The performance tests can be carried out in the sapphire cell (Figure 2.10) or the stainless steel cell (Figure 2.12). A sapphire rocking cell consists of four individual cells enclosed in stainless steel (Figure 2.11) [14].

Figure 2.10 Rocking cell equipment [14].

Figure 2.11 The sapphire cell [14].

Another type of rocking cells was made from SS316 (for sweet testing) or a Hastelloy C276 (for sour testing) as illustrated in Figure 2.12. Each cell contains an SS316 (for sweet

testing) or glass (for sour testing) ball which freely rolls inside the horizontal leg when the cell is rocked.

Small cells or test tubes that contain mixtures of deionized water (DI)/KHIs solution are pressurized with gas mixture. Then, the cells are located in the cooling bath and rocked. A ball in each cell will not be moved after the cell is plugged with hydrates [12]. Pressure and temperature are recording while testing to determine condition of hydrate formation. Hydrate formation temperature is identified by dropping of pressure inside the cell because of the gas is entrapped within the ice-like cavities. Hydrate formation temperature can be determined by dropping pressure point. Hydrate formation can be observed visually as well [14]. The time when liquid becomes cloudy and/or the time when gas consumption occurred is called the induction time. The study of THF hydrate and natural gas hydrate can be conducted in rocking cells. This equipment is simple but effective natural gas hydrate test apparatus for AAs [12].

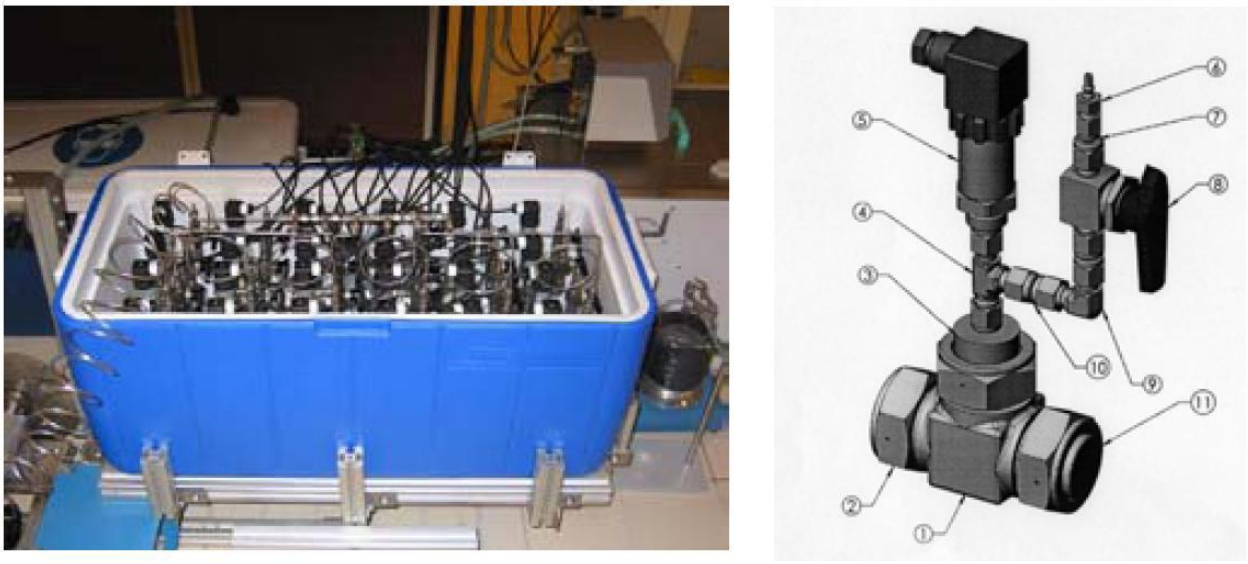


Figure 2.12 Rocking cells used by Shell GSI. The photo at the right shows an individual cell and the main parts, which are comprised by: the 1'' tee (1), the end-nuts (2), the pressure transducer (5), a HP quick-connect gas inlet (6), a ball valve (8) and O-ring tightened blind flanges (11). The picture at the left shows the whole cell that contains 24 cells, as it is mounted to the seesaw [35].

2.5.4 Circulating loop

A complicated piece of equipment used to simulate real field flow conditions is the vertical placed pipe-wheel or loop-wheel [21]. The pipe usually has a diameter of about 1-3 in and has window for visual observation. It is pressurized and rotated in a cooling bath [12]. Recently, mini loops or micro loops have been developed. A stainless steel pipe loop and a gear pump with a mixing tank for inhibitors are used to circulate a mixture of water and liquid hydrocarbon through the loop. The pipe loop is divided to numerous parts where each part has a thermometer and a differential pressure meter. The pressure drop over a single part (hydrate formation) is allowed and monitored by the pressure meter [32]. The micro loop testing, as shown in Figure 2.13, has been tested to match the conventional loop. It is smaller in size, simpler to operate and easier to maintain. Moreover, it is easy to disassemble and clean [21].

High pressure loops are most used today with a natural gas, condensate, or oil and an aqueous phase. They can range from the mini loop such as ¼ in (diameter) to the full scale pilot loop of 4 in (diameter) or more. The limitation of this equipment is that the pump can crush hydrates making AA experiments difficult to interpret [12]. Examples of a flowloop that are larger than miniloop are presented in Figure 2.14 and 2.15.

Figure 2.13 A micro loop hydrate testing apparatus [21].

Figure 2.14 A wheel-shaped flowloop (Sintef, Norway) [19].

Figure 2.15 The "Lyre loop" multiphase flowloop for the study of hydrates in pipelines at IFP (French Petroleum Institute) near Lyon, France [19].

2.6 Classes of KHIs

Several water-soluble polymers have been shown to work as KHI. They prevent nucleation of hydrate crystals by preventing the growth of gas hydrate embryos to the critical nuclear size. At that point, the Gibbs free energy becomes negative ($\Delta G<0$). This means the process of hydrate crystallization goes spontaneous [36]. There are two main keys in KHIs polymer. The first key factor is requirement of functional group which is typically amide groups. They have hydrogen-bond with water molecules or gas hydrate particle surface. The second, a hydrophobic group which is adjacent to or bonded directly to each of the amide groups [4]. KHIs polymer consist of polyethylene strands with suspended lactam (a N atom and a C=O group) chemical rings which are approximately spherical in shape and polar.

The first KHIs to be discovered was polyvinylpyrrolidone (PVP) at Colorado School of Mines (CSM) in 1991 [12]. PVP is a five-ring of the series of polyvinyllactams. PVP without any synergists has subcooling around 3-4^{o}C (5.4-7.2^{o}F) at 70-90 bar.

The chemical structures of PVP, PVCap and vinyl caprolactam copolymer are shown in Figure 2.16 and 2.17.

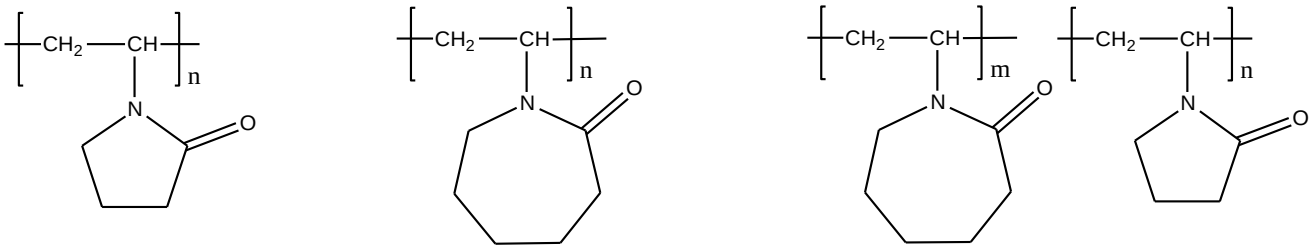


Figure 2.16 Poly-N-vinyllactam polymers: polyvinylpyrrolidone (PVP), polyvinylcaprolactam (PVCap) and vinylpyrrolidone:vinylcaprolactam copolymer (VP:VCap) [4]**.**

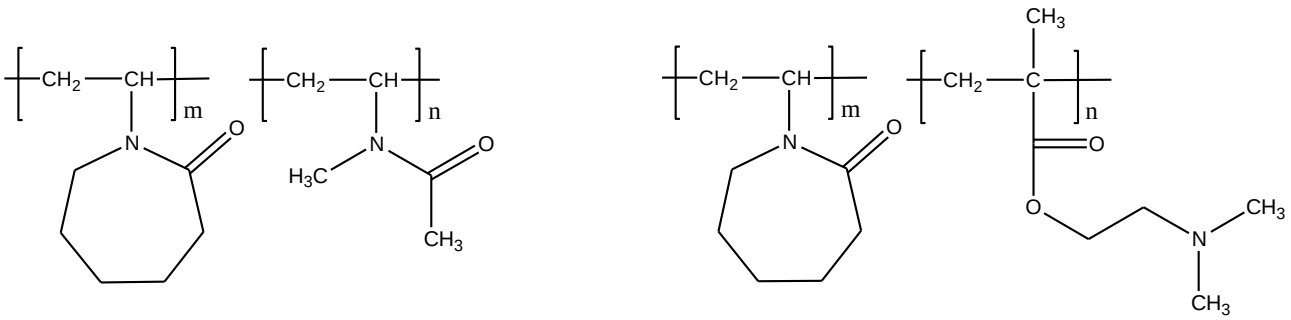


Figure 2. 17 N-methyl-N-vinyl acetamide: vinyl caprolactam copolymer (VIMA:VCap) and vinyl caprolactam:dimethylaminoethylmethacrylate copolymer (VCap:DMAEMA) [4].

The key of these KHIs polymer performance is that they adsorb onto the surface of growing hydrate particles with the polymer pendant group as a "pseudo-guest" in a hydrate cavity at the crystal surface.

The pendant lactam groups act to "anchor" the polyethylene polymer backbone to the $5^{12}6^{4}$ hydrate trap surface. The polymer will not allow dislodge. The key properties of KHIs

are (1) that the pendant group on the polymer shall fit into a growing of $5^{12}6^4$ cage and (2) the pendant groups spacing on the polymer backbone have to match the spacing of the growing $5^{12}6^4$ cages on the hydrate crystal surface [15].

The development of current KHIs came originally from a research on an anti-freeze protein (APFs) or an ice-structuring protein (ISPs) (Figure 2.18) that found in some species of fish, insects, plants and bacteria. APFs or ISPs compose of polypeptides, they bind to small ice crystals to inhibit growth and re-crystallization of ice, which would be fatal to the species. Molecular weight of ISPs are normally about 2-12 kDaltons.

Researcher's general assumption is that the amide and hydroxyl groups in ISPs bind with the ice crystal surface which limit and deform their growth. This requires an appropriate spacing of amide and hydroxyl groups to align with water molecules on the ice surface [36].

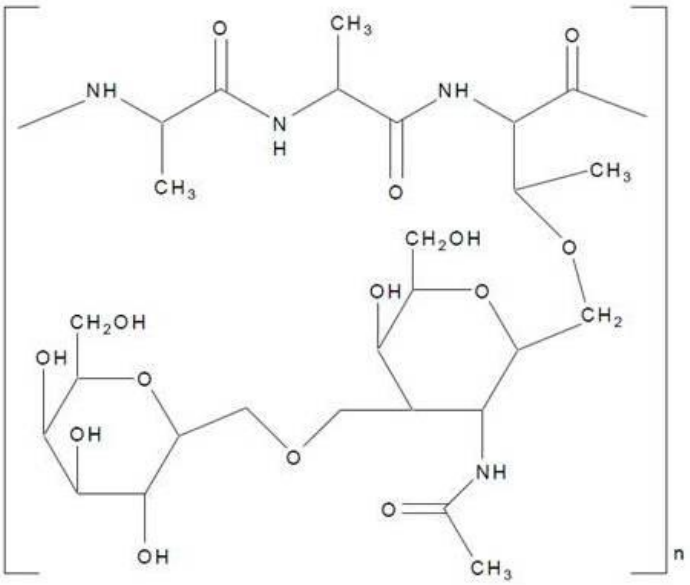


Figure 2.18 Chemical structural of an anti-freeze protein (or ice-structuring protein) from the winter flounder [36].

The system which consists of a high concentration of H_2S or CO_2 will reduce the performance of polymeric KHIs. It relates to the relatively high solubility in water when compared with small hydrocarbon and the fact that these gases are also clatrate hydrate formers.

However, most KHIs field applications are based on polymers from these two classes (1) vinyl lactam polymer or its copolymer, and (2) hyperbranched polyesteramides [4]. The detail of classes of KHIs is given in the literature [36].

2.7 The onset of hydrate formation, t_o and the catastrophic growth process, t_a

A performance of kinetic hydrate inhibitors is typically considered in terms of an induction time. Experiments are usually operated at isothermal and/or isobaric conditions, which are usually stated in the field operation [2]. The process of hydrate formation can be divided into three steps; these are a conduction period, a slow growth period and a catastrophic fast growth period as show in Figure 2.19 [37]. Isothermal test (but not for constant cooling), kinetic hydrate inhibitors delay the nucleation and typically the growth of gas hydrates as well [34]. The induction time (the nucleation delay time) is the most critical factor. It depends on a subcooling (ΔT) in the system. The subcooling is usually evaluated as the driving force for the hydrate formation [2, 34]. When the subcooling is high, the induction time will be low. An absolute pressure is also an important factor [34].

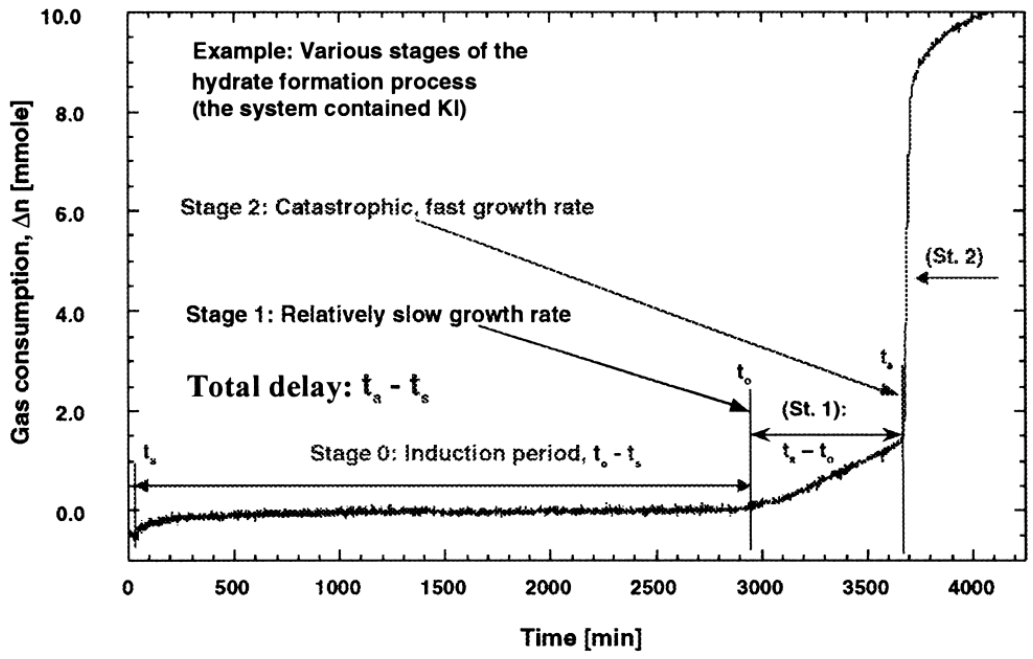


Figure 2.19 The three main steps of the hydrate formation process. [37]

The induction time is defined as the time from the start of stirring in an experiment until the first sign of hydrate formation or the first sign of gas consumption by hydrate formation. The induction time can be evaluated by an equation presented below [37, 38].

$$t_i = t_o - t_s \quad (3)$$

t_i = induction time

t_o = onset time for hydrate formation in the system

t_s = time from the start of stirring, defined zero time for the experiment

The slow growth period is measured by the onset time, t_o, until the onset of catastrophic growth process, t_a. Thus, the definition of the total delay, t_{tot}, at the catastrophic process is [37]

$$t_{tot} = \text{induction + slow growth} = t_a - t_s \quad (4)$$

Since hydrae nucleation is a stochastic process, the induction time has variable values. In order to avoid the variability, repetition is necessary for each test condition. The inhibitors usage ranged from 0.5 wt% to 5 wt% and the concentration at 2.5 wt% is the most frequently used [39].

2.8 The cooling methods

The performance of kinetic hydrate inhibitors test on gas hydrate can be used in various ways such as

i. The isothermal method [2, 37, 40-44]
ii. The constant cooling method [38, 45] and
iii. The ramping method [31, 46].

These three methods are discussed in section 2.8.1-2.8.3 below.

2.8.1 The isothermal method (constant temperature)

In the isothermal method, fluids are cooled down to a certain subcooling with or without stirring. This condition is maintained at this temperature and held until hydrates form. The start time of the pressure drop is the induction time (t_i) or hold time, although nucleation may have occurred before but it is not detected. The total time, t_{tot} , can be also determined. t_a is the time when a hydrate plug forms. The period between t_i and t_a is interval that hydrate crystals are slowly growing (Figure 2.20). It is called the slow growth time, St-1 [34].

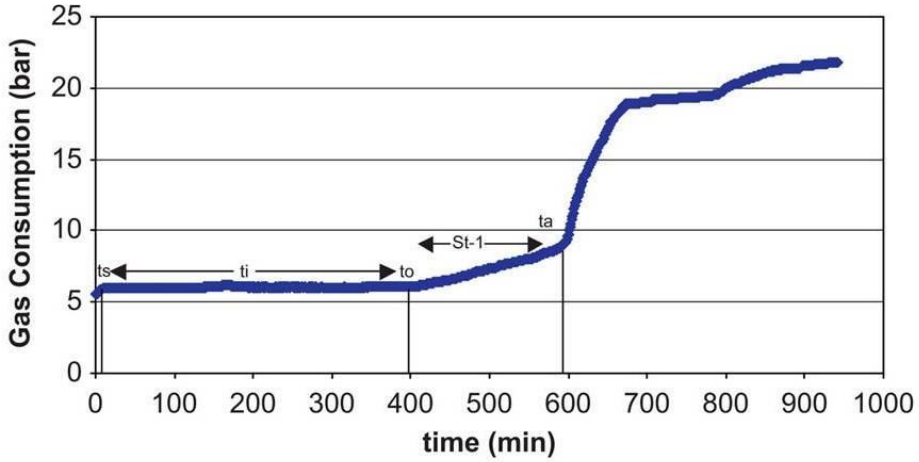


Figure 2.20 A tested result of the isothermal KHI method (Luvicap 55W from BASF, containing a 1:1 vinylcaprolactam:vinyl pyrrolidone copolymer) [34].

2.8.2 The constant cooling method

This method is performed by cooling down with agitation to very low temperature (high subcooling) as illustrated in Figure 2.21. If this method is executed in a closed-system over a short period of time (such as several ^{o}C/h rate), t_i (induction time) will be difficult to define because the pressure is also dropping while cooling down the fluids [34].

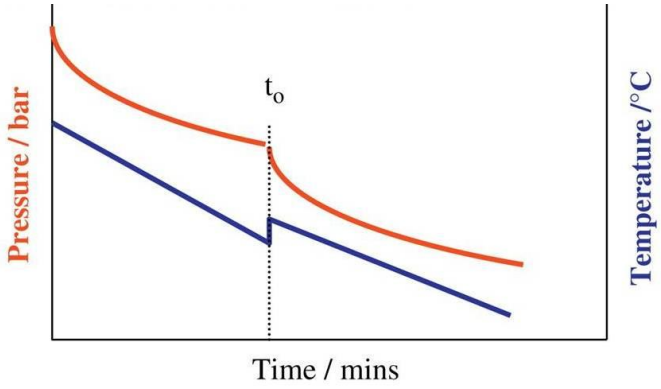


Figure 2.21 The typical graph of a constant cooling KHI method. [34]

A typical graph of pressure and temperature against time from a constant cooling method experiment in a closed vessel is given in Figure 2.21 [34]. Hydrate formation onset (t_o) can usually be observed by the sudden drop in pressure since gas uptake, as well as a temperature spike due to the heat generated by the exothermic crystallization reaction of hydrate formation [34, 39].

2.8.3 The ramping method

This method is run by stepwise cooling. By cooling the fluids down to a certain subcooling then held at this step for a few hours, after that rapidly decrease temperature to a higher subcooling and held again. This ramping step can be repeated again for several times until hydrate have formed. (Figure 2.22)

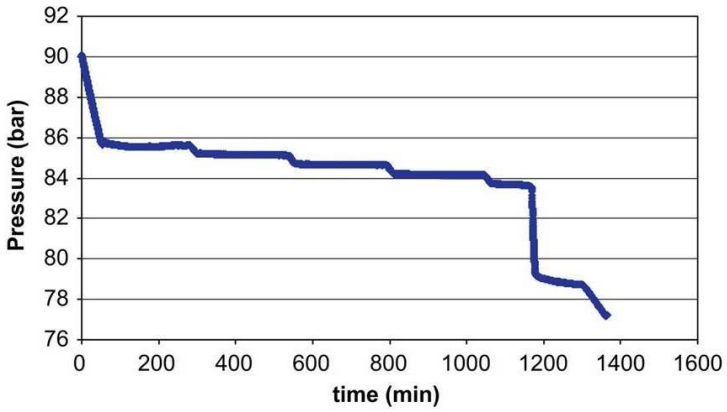


Figure 2.22 A ramping KHI test graph [34].

3 EXPERIMENTAL

3.1 Chemicals and gas

- Inhibex 101 (low Mw poly(N-vinylcaprolactam) PVCap in BGE)
- Inhibex 501 (Poly VP/Vcap in BGE)
- Inhibex 713 (Poly VP:VCap:DMAEMA terpolymer in EtOH)
- Luvicap 55W (VP:VCap copolymer)
- Luvicap EG (low Mw PVCap in MEG)
- Luvicap Bio (Poly VCap copolymer inBGE)
- PNIPAM 10k (poly(N-isopropylacrylamide))
- AP-1000 10k (acryloylpyrrolidine)
- Paspartamide (A polyaspartamide-based product)
- Casein Peptone Plus
- Hybrane (hyper-branched polyesteramides)
- PVP 30k (poly(N-vinylpyrrolidone)s)
- PVP 120k
- PVP Plasdone k-12
- PVCap 8.5k
- PVCap 12k
- PVCap 60k
- Pyroglutamate
- Inhibex Bio 800
- Antaron P904 (Agrimer P904 or butylated PVP)
- VIMA (N-methyl-N-vinylacetamide)
- TBAB (Tetrabutylammonium bromide)
- VIM (Vinylimmidazole)
- Sodium chloride (NaCl)
- Synthetic Natural Gas (SNG). The composition of SNG is shown in Table 3.1.

Table 3.1 The SNG composition.

Component	Concentration (mole %)
Methane	80.4
Ethane	10.3
Propane	5.0
Iso-butane	1.65
n-butane	0.72
N_2	0.11
CO_2	1.82

The concentrations of the relevant gas hydrate inhibitors are given in Table 3.2.

Table 3.2 The concentrations of the gas hydrate inhibitors.

Hydrate inhibitor	Concentration (weight %)
Luvicap 55W	53.8 % in water
Luvicap EG	41.1 % in monoethylene glycol (MEG)
Luvicap Bio	40 %
Inhibex 101	50 % in butyl glycol ether (BGE)
Inhibex 501	50 % in butyl glycol ether (BGE)
Inhibex 713	37 %
Inhibex Bio 800	36 %

3.2 The Rocking Cell RC 5 test equipment (PSL Systemtechnik, Germany)

3.2.1 The rocking cell test equipment.

In this experiment, KHIs performance tests are carried out in RC5 equipment. This RC 5 was pre-calibrated by the manufacturer before it was delivered to University of Stavanger (UIS). The set–up of the rocking rig cell test equipment comprises of 5 test cells,

RC5 main unit, control panel with gas booster, vacuum pump, the tempering bath, and PC-accessories with the WinRC software as presented in Figure 3.1.

The booster was used to reach the right pressure when the pressure in the bottle had lower than operational pressure.

The temperature throughout the test can be seen from the WinRC (computer software) or/and directly from the cooling bath.

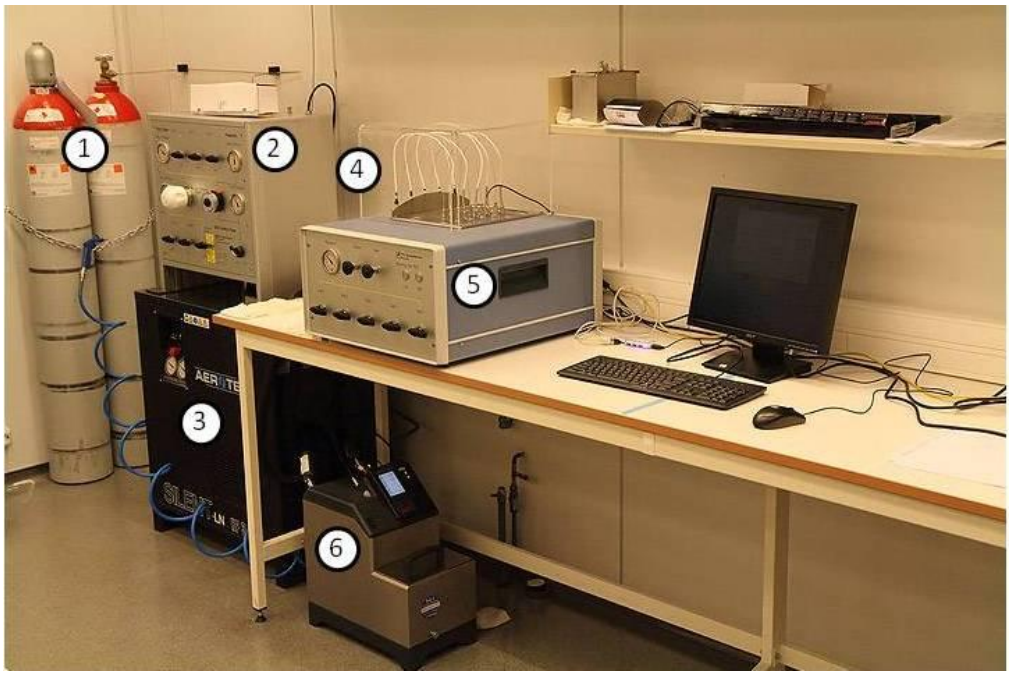


Figure 3.1 The rocking cell test equipment that consists of SNG gas bottle (1), control panel (2), gas booster (3), the protection cover (4), RC5 main unit (5), and the tempering bath (6).

RC 5 base unit composes of 1. Pressure supply tubes (peek-tube), 2. Temperature sensor connectors and 3. Test cells that each of test cell consists of the cell body with the temperature sensor, nut bolts on both sides and a ball (Figure 3.2).

RC 5 has 5 test cells, the volume of each cell is 40 ml, which are able to perform simultaneous runs. The first RC 5 rocking rig uses a magnetic mechanism to fasten the test cells in the cooling bath. Whereas, the new RC5 rocking rig used for this experiment does not have magnets at the bottom of the test cells. Instead, the rocking cells are placed by inserting the fixing rod below each cell into small drill hole on the cell holder in the cooling bath.

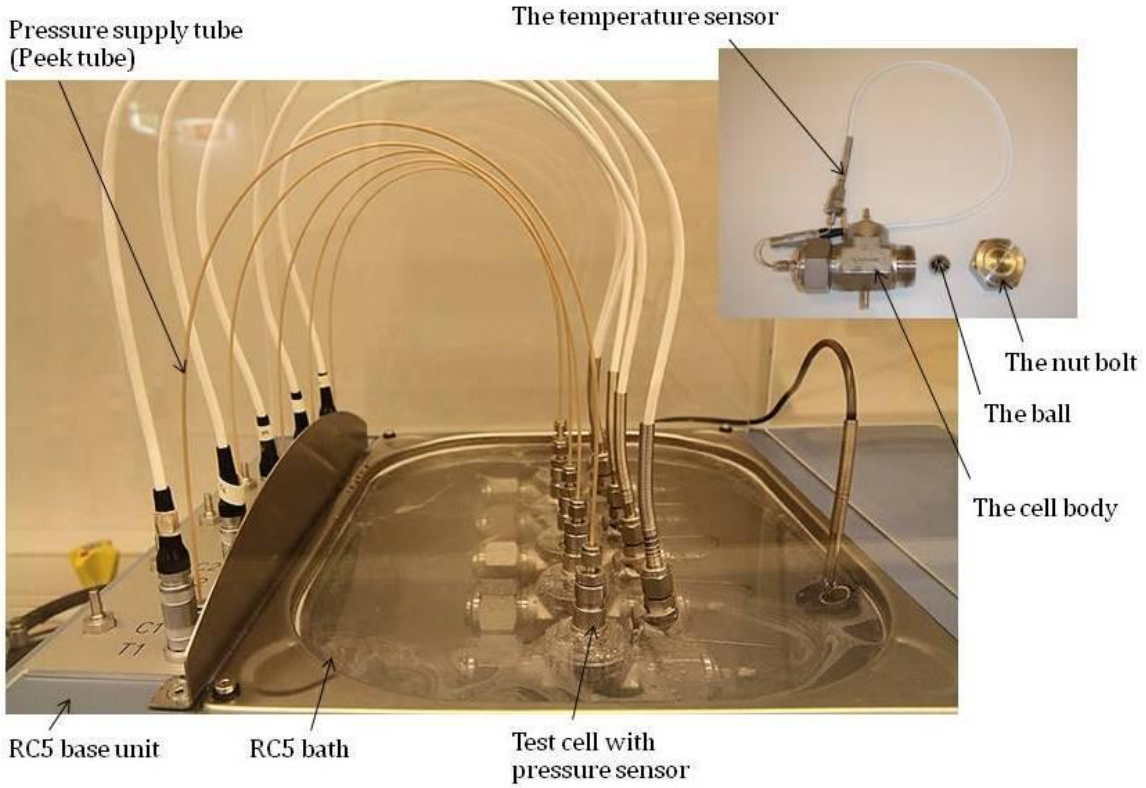


Figure 3.2 The 5 test cells of rocking cell.

The movement of the ball inside the test cell from one side to the other blends the test solution during the rocking. The ball shear forces and turbulences from this movement is the simulation of fluid flow situation in the pipeline**.**

3.2.2 The test procedure

The preparation of the chemical experiment and filling of the steel cell is performed using the same procedure in all high pressure experiment:

1) Preparing KHIs solution

The chemicals to be tested are dissolved in aqueous fluid (0.5% NaCl solution or de-ionized water) to the desired concentration which are 2500 and 5000 ppm.

2) Starting the RC5 equipment

a) Turn the tempering bath on.
b) Switch on the RC5 main unit by pressing the button (on) from front panel. Hold for more than 3 seconds to avoid problems controlling the temperature from the WinRC software.
c) Open the software WinRC.

3) Preparing the cells

In the experiment, the cells should be placed on the same platform in the RC5 bath and should use the same ball and screw cap for their body cell every time. The same procedure for preparing of inhibitors and filling of the cells is as follows:

a) Place a ball in a cell before filling the solution to prevent loss of fluid.
b) 20 ml of the aqueous solution is added to each cell. Starting from cell 5 will be easier to place the cells in the RC5 bath. Be careful that the solution may spill through gas inlet tube when the cell tilts.
c) Fasten the screw-cap (nut bolt) of the cell and liquid by hand tight and by spanner respectively to avoid leakages.
d) Set the temperature of cooling bath to 20.5^{o}C, 0.9^{o}C above the hydrate equilibrium temperature, at the pressure conditions to be used in the test (76 bar). The results from experiment using the RC5, SNG, and DI water in 2011 gave the subcooling around 19.8^{o}C at 77 bar (calculated by PVTSim software from Calsep, Denmark) [47].
e) Use the provided pressure supply tube (Peek tube) to connect the test cell to the RC5.
f) The cell is placed into the bath containing mainly water with a small amount of glycol. A cell can be mounted on the axis in the RC5 bath by inserting the fixing rod of the cell to the corresponding drill hole in the platform. Push and move the cell a little to ensure that the pin on the platform is locked to the drill hole on the cell.

g) Connect the temperature sensor of the cell to the corresponding socket on the RC5.

h) Place the protection cover over the bath until finished from testing for safety.

4) Flushing the cells

There are two methods for flushing the cells to remove air: a) usage of 30 bar twice or b) usage of 2-3 bar with vacuum pump. The second way is preferred in order to save time and gas. These methods is described in a) and b).

a) Flushing the cells twice at about 30 bar pressure.

- Make sure the *"outlet*" valve is closed.
- Open the gas supply and open the valves of test cells. Purge SNG into the cells around 30 bar pressure. The pressure of the test cells can be monitored either from WinRC5 software in the pressure display and/or from pressure gauge at the front panel of main RC5 unit. Slowly open the *"inlet*" valve of the test cell because if too much pressure is let in at once, it can cause foaming in the cell.
- Close the *"inlet*" valve when the cell pressure has reached 30 bar.
- Start rocking for 5-10 minutes by press at *"the start motor*" button. If some cells leaked, bubble will be seen in the RC5 bath and/or pressure drop at the WinRC software.
- Stop the motor when rocking is completed.
- Depressurize the cells by opening the valves of the cells and slowly open *"outlet*" valve. Gas outlet speed is typically lower than 1 bar per second due to some chemicals will increase foam production at high gas outlet speed.
- Close the valves when the pressures in the cells are 0 bar.
- Repeat the procedure for the second time.
- Start rocking 5-10 minutes again when the pressures in the cells are 0 bar in order to release any pressure left.
- Open the valves of cells to release the pressure left.

b) Flushing the cells around 2-3 bar by using vacuum pump for depressurization.

- Make sure the *"outlet*" and *"inlet*" valve are closed.
- Turn the valve at the outlet pipe to the vacuum pump line. For safety concern, this valve should be pointed to the ventilation channel when vacuum pump is not used.
- Open the valves of the cells.
- Turn on the vacuum pump.
- Open the *"outlet*" valve and let it pump ca. 5-10 minutes. (Vacuum pump can remove 99% of air from the cells as the instruction manual)
- Close the *"outlet*" valve.
- Turn off the vacuum pump.
- Purge SNG into the cells ca. 2-3 bar and use the same procedure in method a).
- Close the valves after the pressures in the cells are 0 bar.
- Rock the cells for 5-10 minutes.
- Use vacuum pump again by open the valves of the cells. Turn on the vacuum pump, open the *"outlet*" valve and let it pump ca. 5-10 minutes.
- The SNG ca. 2-3 bar in the cells is released into the laboratory room.
- Close the *"outlet*" valve.
- Turn off the vacuum pump.
- Turn the valve at the outlet tube to the ventilation line.

The test cells are ready for pressurization process.

5) Pressurizing

a) Make sure all the valves are closed.
b) Open the gas bottle then open *"gas 1*" valve on control panel and let pressure reach to the required total pressure.
c) Close *"gas 1*" valve.
d) Open *"gas out*" valve
e) Open the cells vales on RC5 main unit.
f) Slowly open the *"inlet*" valve to be filled.
g) Fill the cells with ca. 76 bar of SNG. Monitor the pressure inside the test cells in the pressure display of the software WinRC5.

h) Close the *"outlet"* and *"inlet"* valve of RC5 main unit when the cell pressure has reached 76 bar.
i) Close *"gas out"* valve of the control panel.
j) Close the gas bottle.

In case of SNG gas in the bottle has lower than desire, boosting will be use.

6) Boosting

A control panel with gas booster can be provided to add the test cells with gas. The gas booster is a pneumatic device and can be used to increase the pressure in the test cells. For example, the booster will be used to set an inlet pressure of only 30 bar (in the bottle) to a cell pressure of 100 bar. Boosting usage is given in sections a-c below.

a) Make sure that all valves are closed before starting the booster.
b) Start the booster. An increasing pressure can be seen on the pressure gauge on the RC5 front panel.
c) Turn the booster off when the pressure reaches the desired pressure.

There is high pressure in RC5 main unit for purging SNG into the cells in further experiment.

7) Computer setting

The computer program setting is depended on the different method of cooling. After open WinRC program, the main window will show as in Figure 3.3. This window consists of two sheets (*"Parameter"* and *"Monitor"*) and numeral control sections.

The *"Monitor"* sheet comprises graphs and tables for the measure of pressure and temperature values. The first five rows of the table are the pressure values from cell 1-cell 5 (P1 – P5). The second five rows of the table display are the temperature of temperature sensor for cell 1-cell 5 (T1 – T5) and the sixth rows display is the bath temperature.

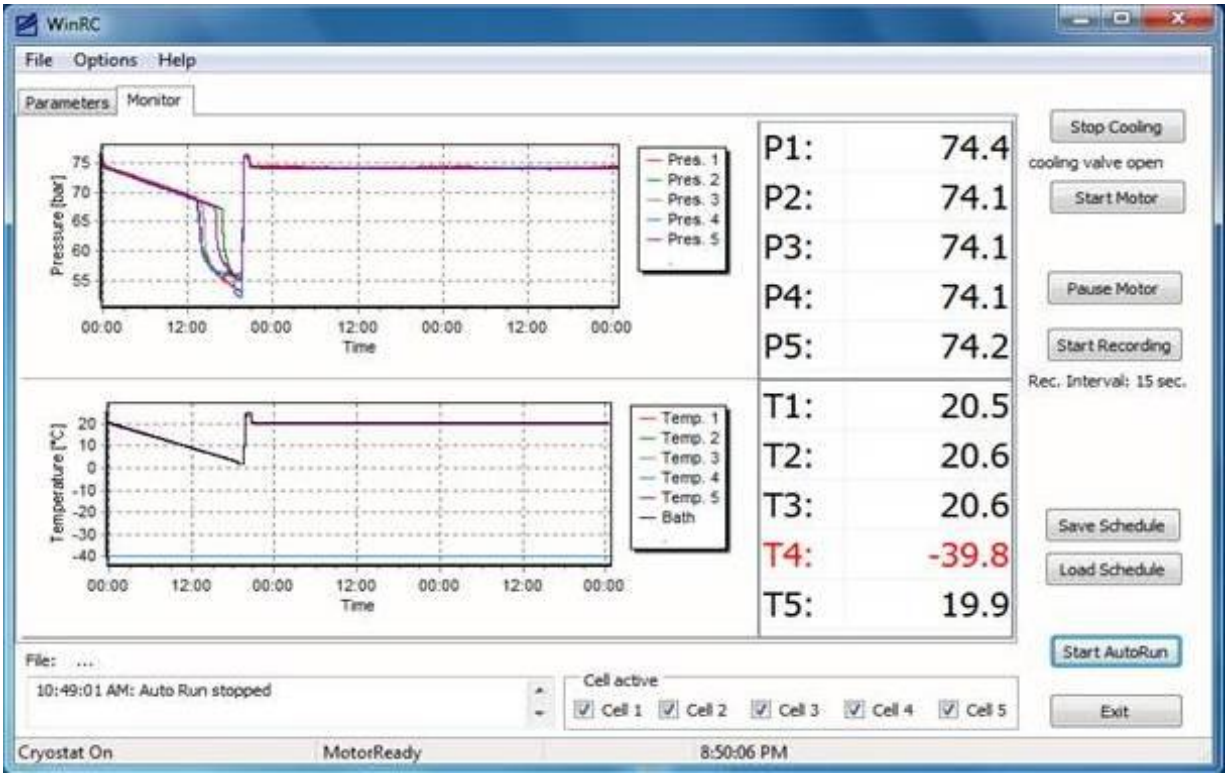


Figure 3.3 The main window of WinRC.

To create a new setting selects the *"Parameter*" sheet in the main window (Figure 3.4). The schedule can be set in a table. Each row of the table represents an experimental step. The settings in Figure 3.4 are used for constant cooling method and the test procedure as follows:

Step 1: The cooling bath temperature is adjusted to 20.5^{o}C which is the start temperature in the experiment. The cell fluids are cooled slowly from 20.5^{o}C to 2.0^{o}C over 18.30 h with a constant cooling rate.

There are two types of command in the *"Command*" column: 1. Flowing and 2. Shut-in. At flowing commands can be set for the rocking rate and angle but for shut-in program only the angle to hold the test cells positions can be set. Standard conditions for this experiment are flowing command, 20 rocking rates (the number of full swings per minutes for the test cell) and 40 angles (the angle that the test cells are tilted). Select the *"Ramp*" to set the target temperature, step width and step duration. In this test, the temperature is decreased by 0.1^{o}C per 6 minutes throughout the step 1.

Step 2: Leave hydrate to grow at 2^{o}C for 1 h. This step usually gives a hydrate plug. For some chemicals which have higher concentrations, more time than 1 h is needed to plug the cells.

Step 3: Heat the cells fast up to 25^{o}C and hold at this temperature for 1 h to melt the hydrate formation.

Step 4: Cool the cells down to 20.5^{o}C for 20 min. This condition is ready for next experiment.

Select *"Start recording"* button.

These four steps are used throughout the experiment.

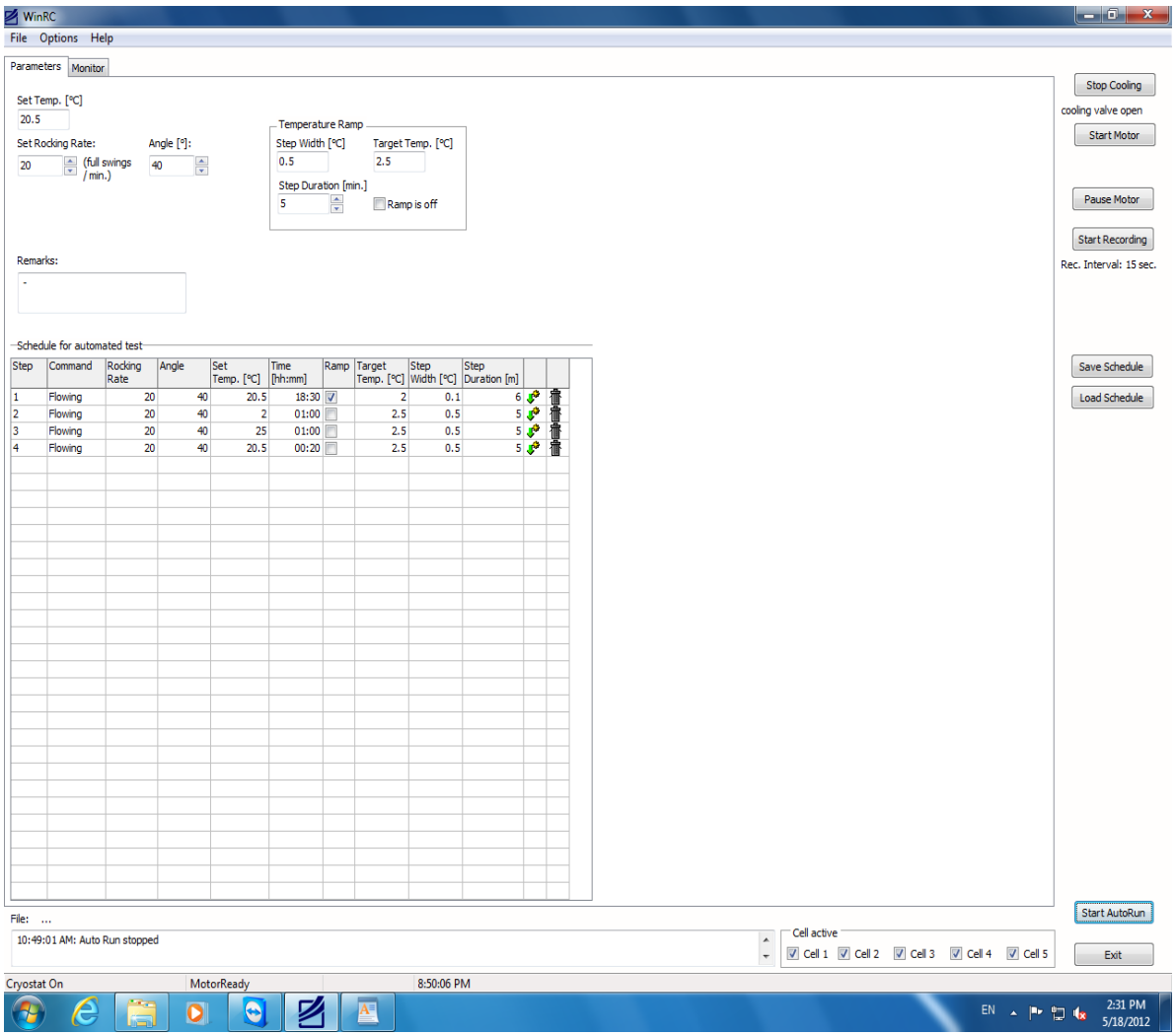


Figure 3.4 The schedule of WinRC.

8) Depressurizing

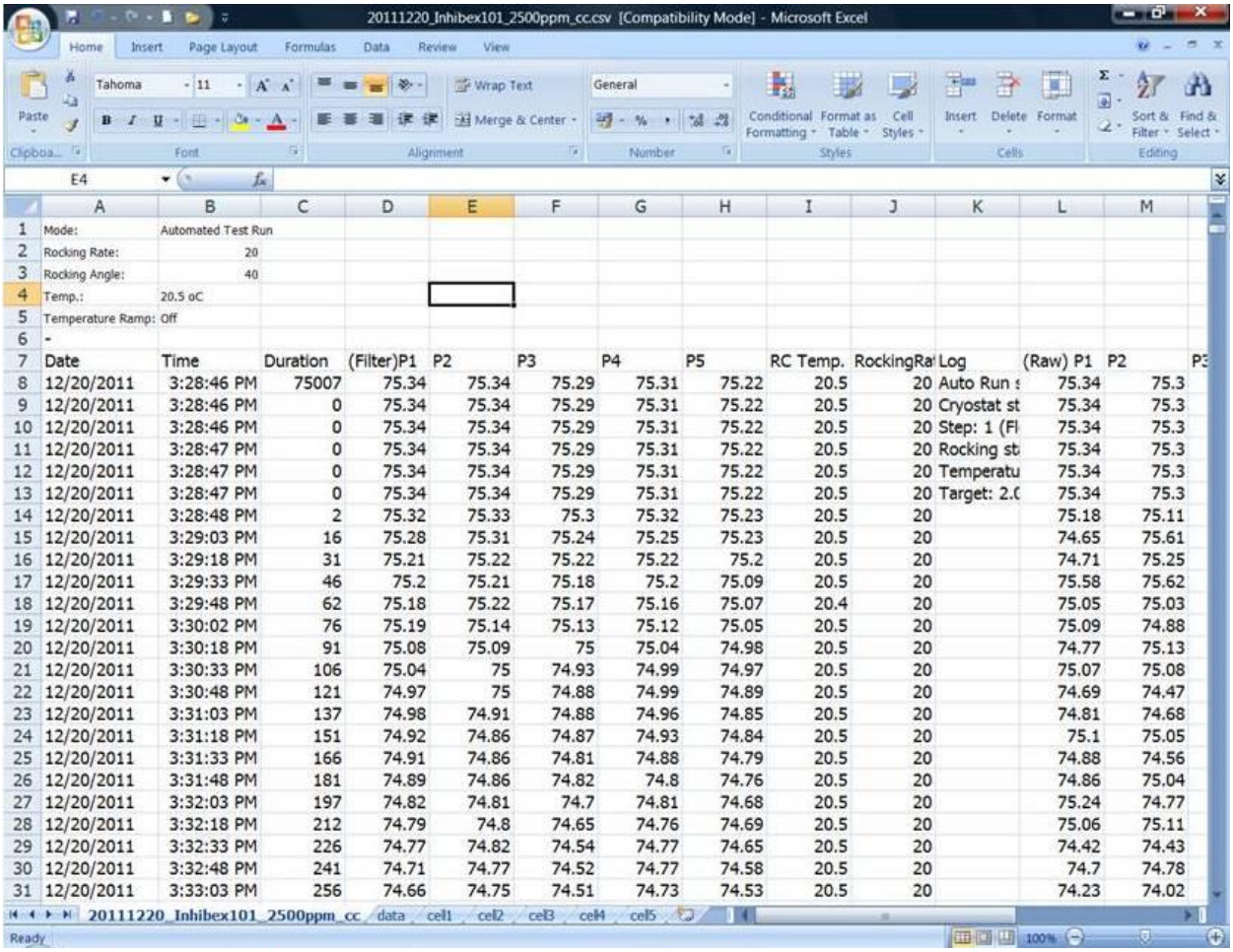
a) To avoid the gas release into the lab room, make sure that the T-valve at the outlet pipe turns to ventilation chamber.
b) Open the cell valves at RC front panel.
c) Slowly open the *"outlet"* valve (around 1 bar per second).
d) Monitor the pressure of the test cells in the pressure display of WinRC software. Close the valve when the pressure is 0.
e) Remove and clean the test cells.

9) Cleaning the cells

a) For safety, the pressure inside the cells should be 0. Opening the test cells when they are still under pressure can lead material damage and/or injures.
b) Disconnect the pressure line from the cell.
c) Disconnect the temperature sensor of the test cell.
d) Remove the test cells from RC5 bath. For simplicity, start from cell 1.
e) Open the screw-cap on one side of the test cell by using spanner.
f) Empty the cell.
g) Clean the cell, the ball and the nut bolt follow by these steps:
    i. Detergent (ex. Zalo) + water
    ii. Tap water (All the detergent should be removed from the cell because zalo is surfactant which may be effect to the test result.)
    iii. Acetone
    iv. Distilled water
h) Dry the cell by using an air gun.

10) Result/Evaluation

Data recorded during the test is saved in a data file (csv-format). The values of this data are separated by semicolon. A data file comprises a file header and a table with the measurement values as illustrated in Figure. 3.5.



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Mode:	Automated Test Run											
2	Rocking Rate:	20											
3	Rocking Angle:	40											
4	Temp.:	20.5 oC											
5	Temperature Ramp:	Off											
6	-												
7	Date	Time	Duration	(Filter)P1	P2	P3	P4	P5	RC Temp.	RockingRa	Log	(Raw) P1	P2
8	12/20/2011	3:28:46 PM	75007	75.34	75.34	75.29	75.31	75.22	20.5	20	Auto Run s	75.34	75.3
9	12/20/2011	3:28:46 PM	0	75.34	75.34	75.29	75.31	75.22	20.5	20	Cryostat st	75.34	75.3
10	12/20/2011	3:28:46 PM	0	75.34	75.34	75.29	75.31	75.22	20.5	20	Step: 1 (Fl	75.34	75.3
11	12/20/2011	3:28:47 PM	0	75.34	75.34	75.29	75.31	75.22	20.5	20	Rocking st	75.34	75.3
12	12/20/2011	3:28:47 PM	0	75.34	75.34	75.29	75.31	75.22	20.5	20	Temperatu	75.34	75.3
13	12/20/2011	3:28:47 PM	0	75.34	75.34	75.29	75.31	75.22	20.5	20	Target: 2.0	75.34	75.3
14	12/20/2011	3:28:48 PM	2	75.32	75.33	75.3	75.32	75.23	20.5	20		75.18	75.11
15	12/20/2011	3:29:03 PM	16	75.28	75.31	75.24	75.25	75.23	20.5	20		74.65	75.61
16	12/20/2011	3:29:18 PM	31	75.21	75.22	75.22	75.22	75.2	20.5	20		74.71	75.25
17	12/20/2011	3:29:33 PM	46	75.2	75.21	75.18	75.2	75.09	20.5	20		75.58	75.62
18	12/20/2011	3:29:48 PM	62	75.18	75.22	75.17	75.16	75.07	20.4	20		75.05	75.03
19	12/20/2011	3:30:02 PM	76	75.19	75.14	75.13	75.12	75.05	20.5	20		75.09	74.88
20	12/20/2011	3:30:18 PM	91	75.08	75.09	75	75.04	74.98	20.5	20		74.77	75.13
21	12/20/2011	3:30:33 PM	106	75.04	75	74.93	74.99	74.97	20.5	20		75.07	75.08
22	12/20/2011	3:30:48 PM	121	74.97	75	74.88	74.99	74.89	20.5	20		74.69	74.47
23	12/20/2011	3:31:03 PM	137	74.98	74.91	74.88	74.96	74.85	20.5	20		74.81	74.68
24	12/20/2011	3:31:18 PM	151	74.92	74.86	74.87	74.93	74.84	20.5	20		75.1	75.05
25	12/20/2011	3:31:33 PM	166	74.91	74.86	74.81	74.88	74.79	20.5	20		74.88	74.56
26	12/20/2011	3:31:48 PM	181	74.89	74.86	74.82	74.8	74.76	20.5	20		74.86	75.04
27	12/20/2011	3:32:03 PM	197	74.82	74.81	74.7	74.81	74.68	20.5	20		75.24	74.77
28	12/20/2011	3:32:18 PM	212	74.79	74.8	74.65	74.76	74.69	20.5	20		75.06	75.11
29	12/20/2011	3:32:33 PM	226	74.77	74.82	74.54	74.77	74.65	20.5	20		74.42	74.43
30	12/20/2011	3:32:48 PM	241	74.71	74.77	74.52	74.77	74.58	20.5	20		74.7	74.78
31	12/20/2011	3:33:03 PM	256	74.66	74.75	74.51	74.73	74.53	20.5	20		74.23	74.02

Figure 3.5 The sample data file of Inhibex 101 at concentration 2500 ppm (part).

The onset of hydrate formation is determined by the beginning of the deviation from the constant pressure drop due to the decrease of temperature. The temperature at this point is recorded (To). Whereas the temperature at the fast catastrophic hydrates formation (Ta) takes place at the start of the dramatic pressure drop. An example of the data recorded has shown in Figure 3.6.

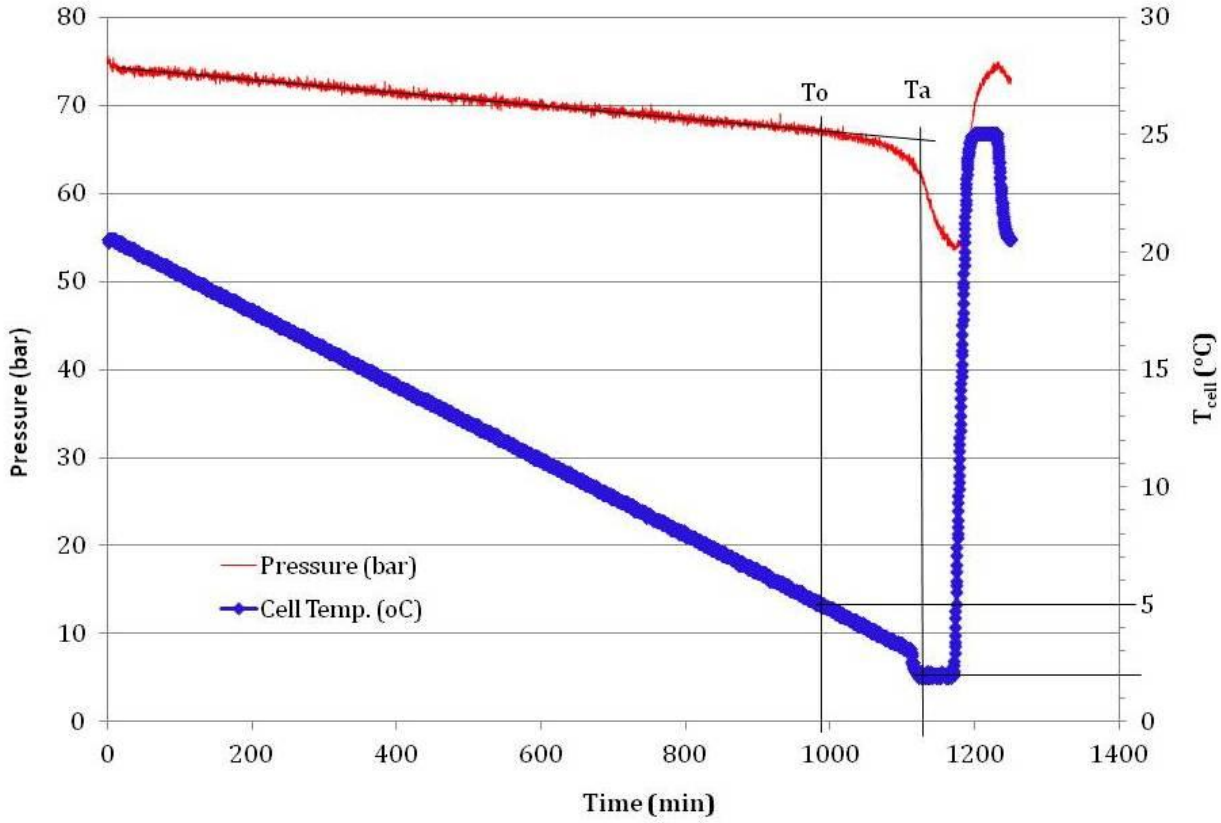


Figure 3.6 A graph of pressure and temperature vs. time of 2500 ppm Inhibex 101 with constant cooling method.

Pressure and temperature inside the test cells are recorded throughout the experiment. In Figure 3.6, a blue color line showed the temperature data. This temperature can be read from the right of Y-axis. The red line on the top represents pressure value. At the point that pressure start to deviate from a black tiled line, the pressure, time (t_o) and temperature (T_o) is around 67 bar, 970 minutes and 5^{o}C respectively. Fast pressure drop occurs after ca. 1100 minutes (t_a) at pressure and temperature (T_a) about 63 bar and 2^{o}C respectively.

3.3 Standard parameter

Standard parameter is used in this experiment is given in Table 3.3.

Table 3.3 Standard parameter

Parameter	Value
Volume of solution	20 ml
Rocking rate	40 rocks per minute
Rocking angle	40^{o}
Concentration	2500 ppm and 5000 ppm
Rocking ball	Steel ball

4 RESULT AND DISCUSSION

The following discussions are experimental results, which are categorized by the effects of various parameters and the study objectives. This study was performed to determine the average onset temperature (T_o) and catastrophic hydrate formation temperature (T_a) of KHIs by using rocking cell. All of the results can be seen in Appendix A.

4.1 Effect of different RC5 on KHIs performance

To verify and validate the results of a new rocker rig instrument, the comparison between the RC5-2012 and the RC5-2011 was used in this experiment. The RC5-2011 equipment has been available in UIS since 2011. Both of RC5s are the same model but they have a few internal differences. The old one has magnet on platform in the RC5 bath and under the cell body to fasten them together, but the new one does not.

The results of the KHIs performance tests are given in Table 4.1.

Table 4.1 The effects of different RC5 on gas hydrate formation with several KHIs.

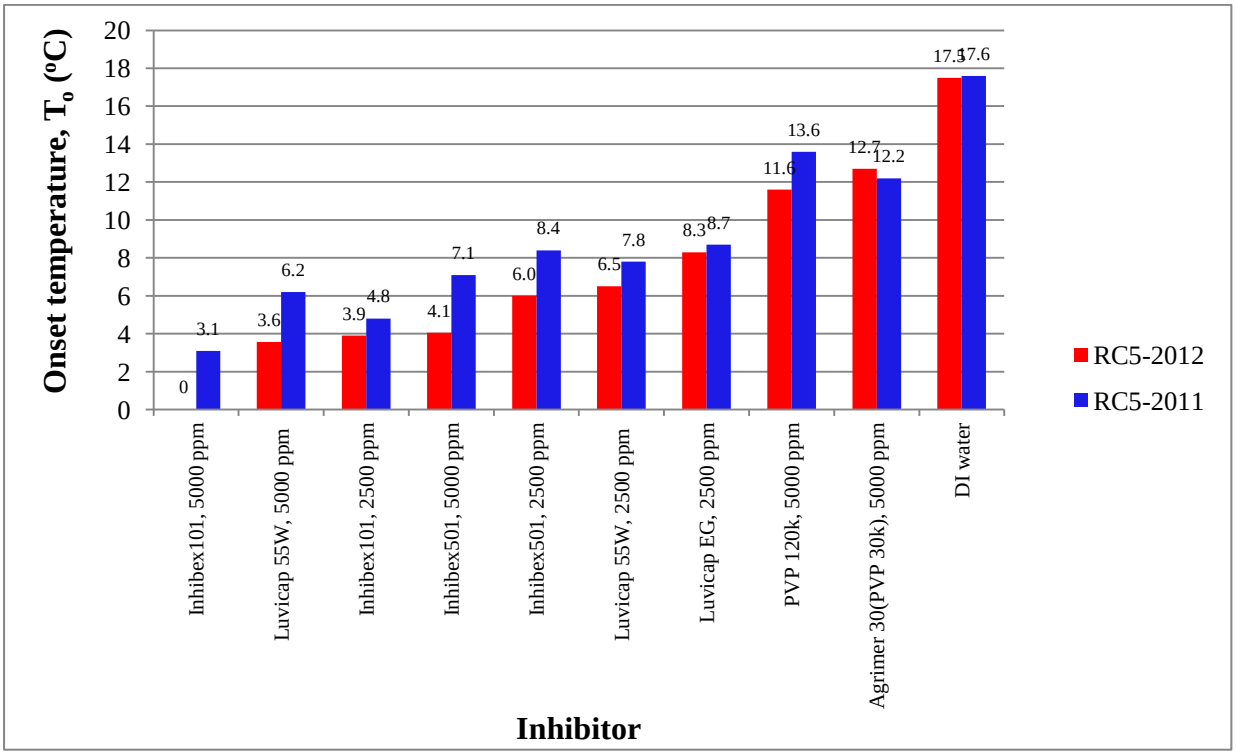
Inhibitor, concentration	Average T_o/T_a (^oC)	
	RC5-2012	RC5-2011
Inhibex101, 5000 ppm	0/0	3.1/-
Luvicap 55W, 5000 ppm	3.6/2.8	6.2/3.4
Inhibex101, 2500 ppm	3.9/2.2	4.8/3.1
Inhibex501, 5000 ppm	4.1/2.3	7.1/2.4
Inhibex501, 2500 ppm	6.0/4.0	8.4/4.9
Luvicap 55W, 2500 ppm	6.5/5.4	7.8/5.8
Luvicap EG, 2500 ppm	8.3/7.7	8.7/8.1
PVP 120k, 5000 ppm	11.6/10.1	13.6/12.9
Agrimer 30(PVP 30k), 5000 ppm	12.7/11	12.2/11.7
DI water	17.5/17.5	17.6/17.6

*The cooling down method was maintained at 2^oC for 1 hour.

**(-) means cannot find the fast growth temperature at 2^oC with 1 hr holding time.

T_o and T_a of inhibex 101 (5000 ppm) are zero because there was no hydrate formation in the new RC5. For the other one, hydrates formed at 3.1°C but it did not plug at 2°C even with an hour holding period at that temperature.

The onset temperatures from experimental are presented in Figure 4.1. The RC5-2012 shows a lower onset temperature than the old RC5 for high performance inhibitors such as Inhibex 101, Inhibex 501 and Luvicap 55W at concentration 2500 and 5000 ppm. Whereas the T_o from new RC5 are nearly the same with the old RC5 for the chemicals which are low performance KHIs.



* The cooling down method was maintained at 2 °C for 1 hour.

Figure 4.1 The onset temperature for KHIs from 2012 and 2011 RC5.

4.2 Effect of the cells conditioning

To understand the effect of the residual internal chemicals from manufacturing, the experiment was conducted with numerous chemicals at the same condition after receiving RC5 (early) and three months later (later). The results are shown in Table 4.2 and Figure 4.2.

Table 4.2 The Average T_o/T_a (^oC) of the cells conditioning with various KHIs.

Inhibitor	Average T_o/T_a (^oC)	
	Later	Early
Inhibex Bio800, 2500 ppm	2.6/-	2.6/-
Luvicap 55W, 5000 pppm	3.6/2.8	4.5/4.0
Inhibex101, 2500 ppm	3.9/2.2	5.2/2.6
Hybrane, 2500 ppm	4.5/4.5	6.0/5.6
Inhibex501, 2500 ppm	6.0/4.0	6.7/4.7
Luvicap 55W, 2500 ppm	6.5/5.4	6.8/5.9
Luvicap EG, 2500 ppm	8.3/7.7	9.1/7.7
DI water	17.5/17.5	18.7/18.7

*****(-) means cannot find the fast growth temperature at 2^oC with 1 hr holding time

From Table 4.2, 2500ppm Inhibex Bio800 formed hydrate at ~2.6^oC but catastrophic hydrate formation did not occur after holding for an hour at 2^oC for both tests. DI water, which does not contain any additive, has started to form hydrate and plug very fast at the same temperature (17.5^oC).

Figure 4.2 shows that almost all of T_o values from the first month (early) are higher than the three month later (later)'s. The reason is impurities from manufacturing and/or losing of the internal cell's roughness [47]. Thereby, T_o and T_a from subsequent experiments were used for comparative studies of other test parameters.

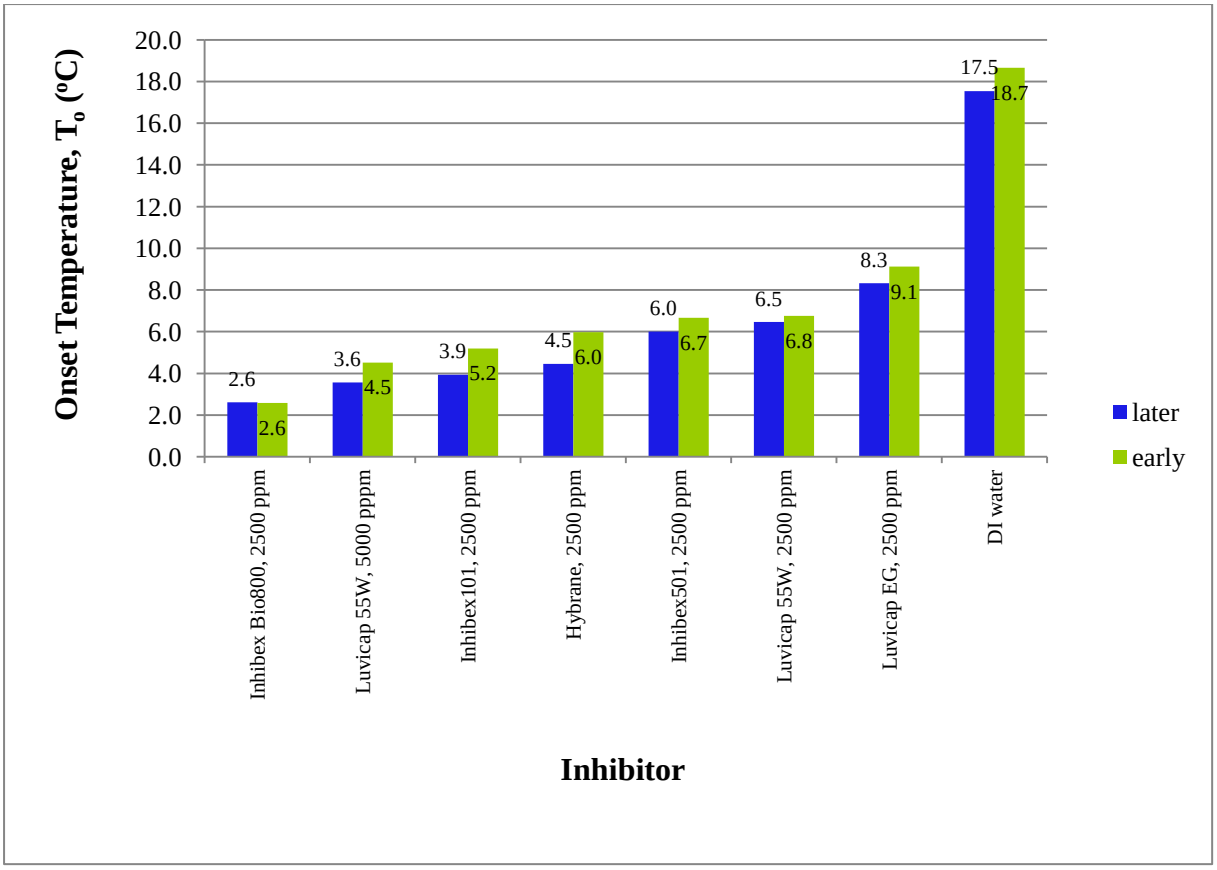


Figure 4.2 Graphic results of the cells conditioning with several inhibitors

4.3 Effect of rocking cell and autoclave apparatus on KHIs performance

Results from the same test conditions (2500 ppm KHI, 76 bar) were compared among RC5, 200 ml. autoclave and 23 ml. autoclave. Quantities of test samples were 20 ml. (RC5), 100 ml. (200 ml. autoclave) and 11 ml. (23 ml. autoclave). The constant cooling method was used to cool the solution down from 20.5°C to 2°C within 18.5 hours with 600 rpm stirring. The results of autoclave test are presented in Appendix B.

Table 4.3 presents the results with numerous KHIs at 2500 ppm concentration. The last constant cooling test was conducted without additive (DI water). The average T_o and T_a are given in the table. For example, for five tested of Inhibex 501, T_o values for hydrate formation were 5.8, 6.2, 6.1, 5.9, and 6.0°C (average 6.0°C) and the T_a values were 3.9, 4, 4, 4, and 4°C (average 4.0°C) indicating good reproducibility. Reproducibility was calculated in percentage by subtracting the result of each cell from the average value of each chemical then dividing with average value. For all the inhibitors tested in this RC5 study, the reproducibility

of T_o and T_a values are ±18-30% scattering. Reproducibility results of this study are given in Appendix C.

For autoclave tests, the deviation from average of T_o and T_a values are ±10-15% in 200 ml steel cell which is better than the smaller size (±20-25%) since the stochasticity of gas hydrate formation being reduced in the larger cell [33]. Small and clean laboratory apparatus are most influenced by the stochastic nature of hydrate formation [4].

Table 4.3 Measured the onset temperature (T_o) and catastrophic hydrate formation temperature (T_a) of several KHIs in rocking cell and autoclave equipment.

Inhibitor	Concentration (ppm)	Average T_o/T_a (^oC) RC5	Autoclave (200 ml)	Autoclave (23 ml)
Inhibex 501	2500	6.0/4.0	6.2/4.9	5.4/3.6
Luvicap 55W	2500	6.5/5.4	6.6/6.0	6.7/6.2
Luvicap EG	2500	8.3/7.7	7.5/6.7	8.0/7.3
PVP Plasdone K-12	2500	11.2/10.5	10.5/10.0	10.0/9.5
Agrimer 30(PVP 30k)	2500	13.1/10.8	12.0/10.9	11.5/6.7
DI water		17.5/17.5	13.3/13.3	11.2/11.2

KHIs performance test in RC5 and autoclave was conducted under 76 bar at 2^oC in DI solution. The results from the high performance KHIs such as Inhibex 501, Luvicap 55W and Luvicap EG were similar with these three equipments whereas the low performance polymers gave difference T_o. From figure 4.3, RC5 presents the highest T_o in the meantime the small autoclave (23 ml) shows the lowest.

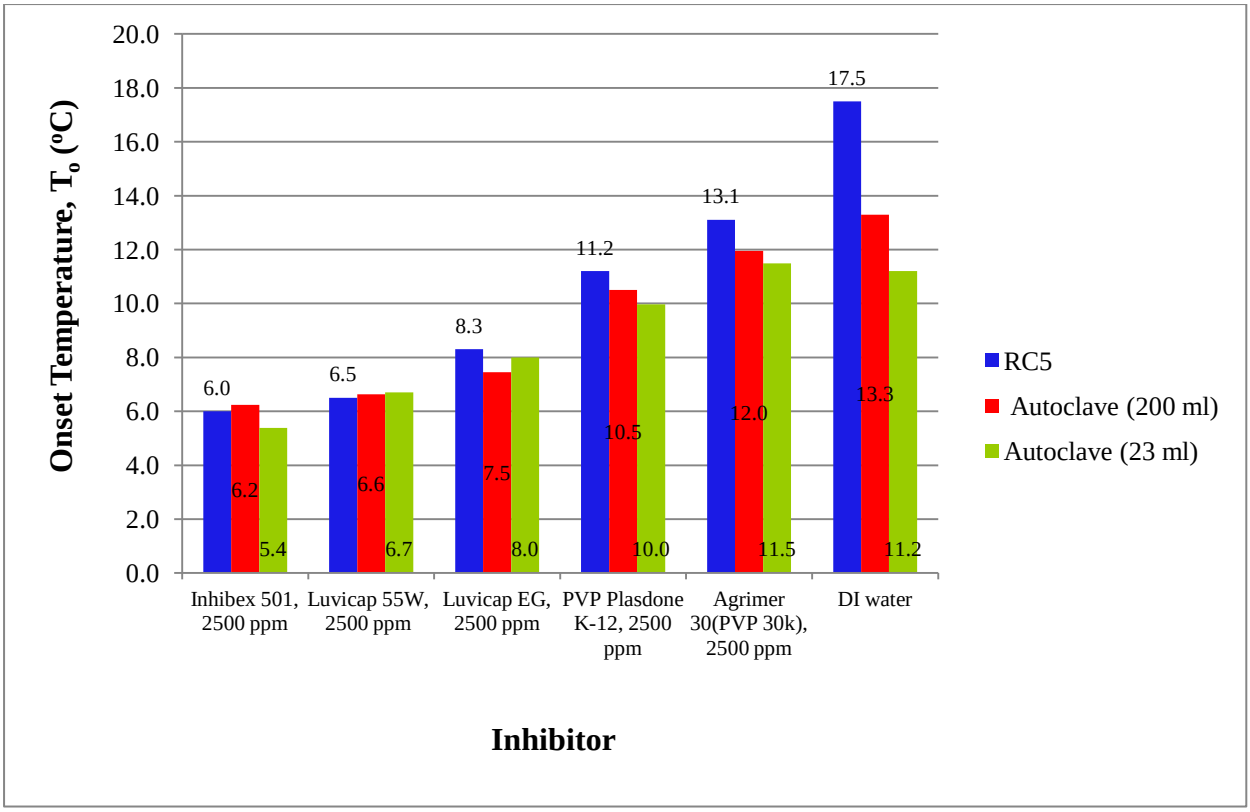


Figure 4.3 Experimental data showing T_o of different KHIs at 2500 ppm with RC5 and autoclave apparatus.

4.4 Effect of magnet on KHIs performance

As mentioned earlier in section 4.1, the old RC5 has strong magnet on platform and cell body. This magnet may have an effect on KHIs efficiency. To understand the effect of magnet, a new RC5 without magnets was ordered from PSL Systemtechnik.

Luvicap 55W at 2500 ppm was used in the test. Figure 4.4 presents five square magnets that were attached on each platform. The test was performed twice, with and without magnets.

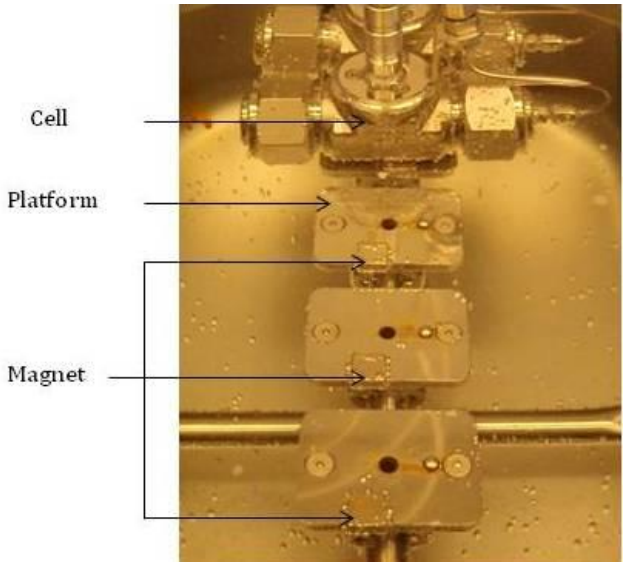


Figure 4.4 The usage and position of magnets in tempering bath of new RC5.

The results are summarized in Table 4.4 and depicted in Figure 4.5.

Table 4.4 Average T_o and T_a of Luvicap 55W at 2500 ppm with/without magnet in RC5 equipment.

Parameter	Average T_o/T_a (^oC)
without magnet	6.5/5.4
with magnet 1	6.0/4.9
without magnet	6.5/5.2
with magnet 2	6.6/5.3

From the test, average T_o of with and without magnet are in the range from 6.0 to 6.6 which are similar. These results show that like the magnet in this experiment has no effect on the onset temperature, but it is not the final conclusion yet regarding magnets. It may be because the position of magnet was not put on the right way, or they need to have a stronger field. More study is necessary to conclude this assumption.

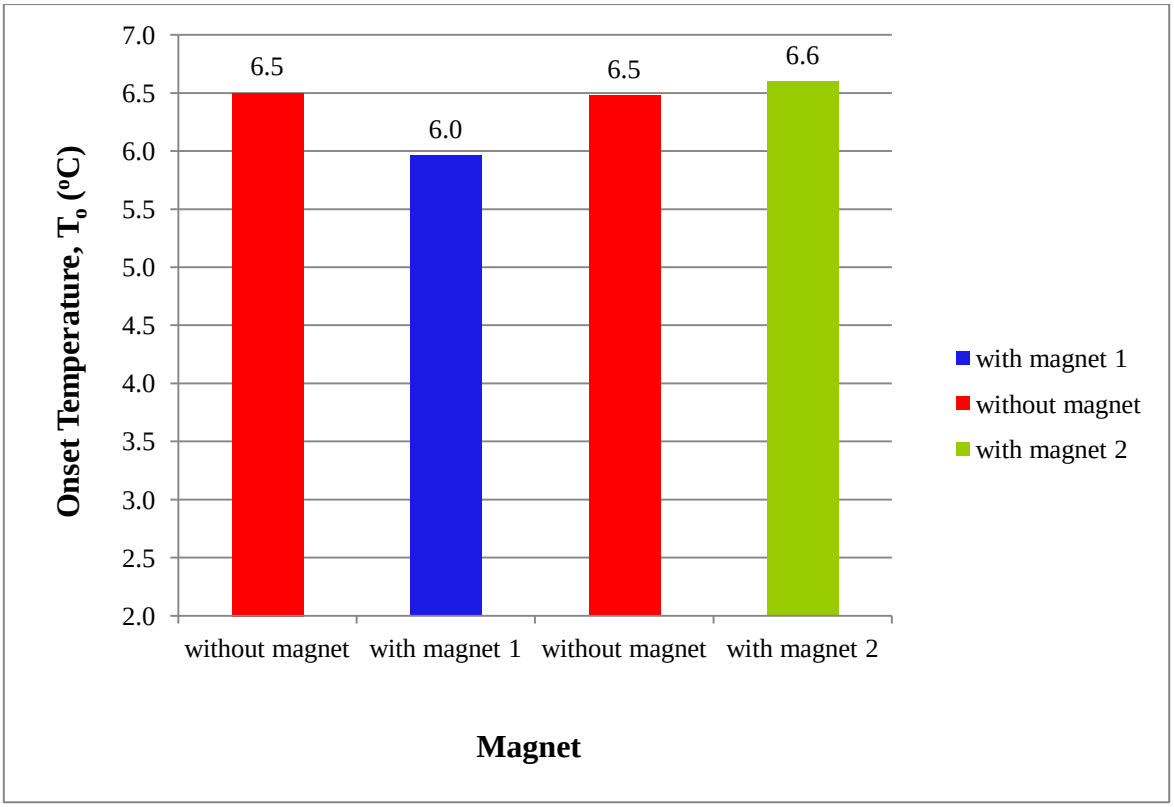


Figure 4.5 The use of magnet results compare with without magnet at 2500 ppm of Luvicap 55W.

4.5 Effect of concentration on KHIs performance

Since the active dose of LDHI such as the actual inhibitor alone is often in the range from 0.2 to 1.0 wt.% (2000-10000 ppm) [36]. Therefore, concentration at 2500 and 5000 ppm have been chosen for this study. Effect of concentration was examined with various chemicals. The efficiencies of KHIs at two concentrations are presented in Table 4.5 and Figure 4.6.

For all of the chemicals, the higher concentration would result in better performance. Onset temperature of hydrate formation slightly decreased when the concentration increased for all additive solutions. At 5000 ppm, Inhibex Bio-800 and Inhibex 101 inhibited the formation of hydrate crystal throughout the test. Inhibitor with higher concentration was not only preventing hydrate formation but also delaying the fast growth of hydrate. For instance, when Luvicap 55W was used, the onset temperature reduced from 6.5°C to 3.6°C and the catastrophic hydrate formation temperature decreased from 5.4°C to 2.8°C at 2500 and 5000

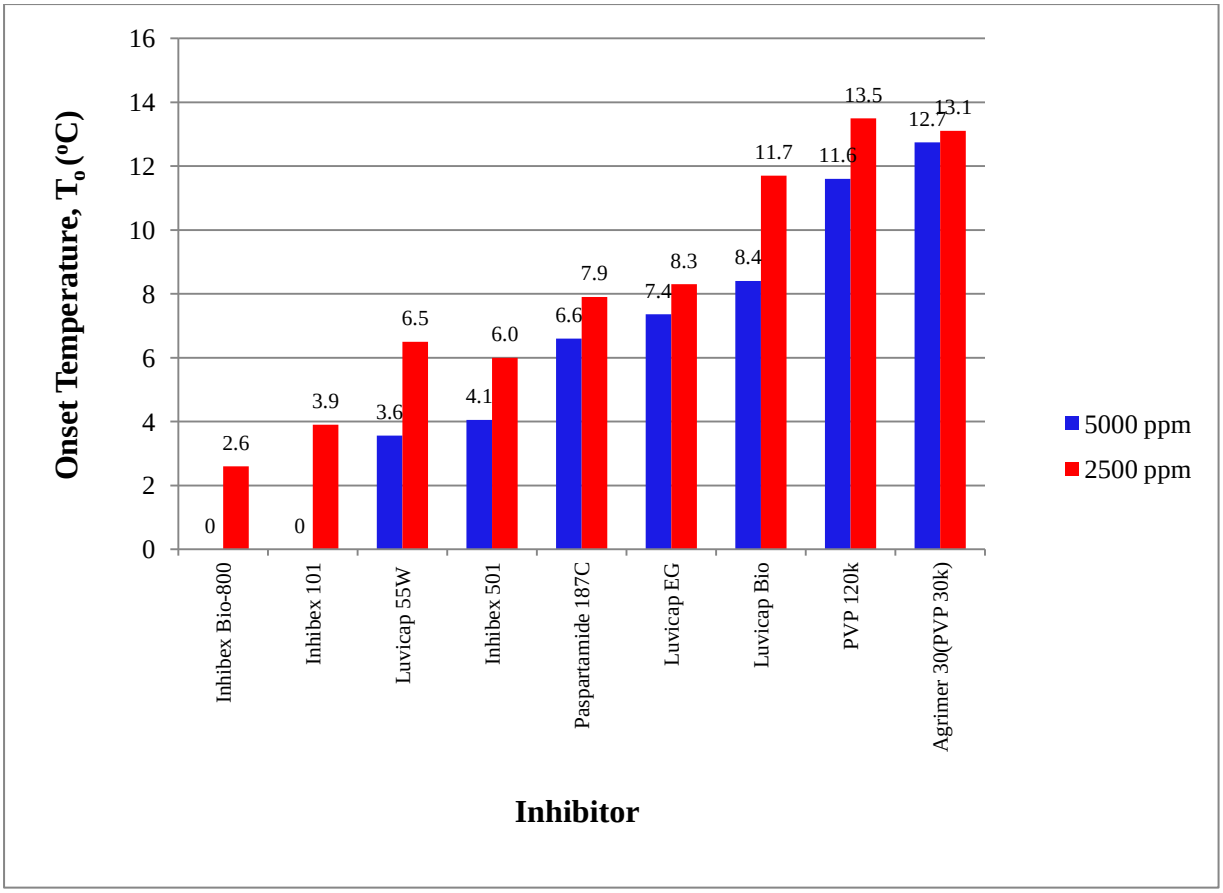
ppm respectively. The reasons are; 1) The more inhibitor in the system, the more water is prevented from participating in the structure of hydrate, thus higher pressures and lower temperatures are required for hydrate formation from the remaining, uninhibited water [15]. 2) The rising of polymer concentration induces a significant increase of solution viscosity [42]. If the viscosity increases, the solubility of gas in water will be decreased.

Table 4.5 Average T_o and T_a of various inhibitors at 2500 ppm and 5000 ppm.

chemical	Average T_o/T_a (^oC)	
	5000 ppm	2500 ppm
Inhibex Bio-800	0/0	2.6/-
Inhibex 101	0/0	3.9/2.2
Luvicap 55W	3.6/2.8	6.5/5.4
Inhibex 501	4.1/2.3	6.0/4.0
Paspartamide 187C	6.6/6.6	7.9/7.6
Luvicap EG	7.4/6.5	8.3/7.7
Luvicap Bio	8.4/8.2	11.7/11.1
PVP 120k	11.6/10.1	13.5/11.2
Agrimer 30(PVP 30k)	12.7/11.0	13.1/10.8

*The cooling down method was maintained at 2^oC for 1 hour.

**(-) means cannot find the fast growth temperature at 2^oC with 1 hr holding time



*The cooling down method was maintained at 2°C for 1 hour.

Figure 4.6 The results comparison of different inhibitors at concentration between 2500 and 5000 ppm

4.6 Effect of adding sodium chloride in the solution on KHIs performance

The most commonly used of THIs classes are alcohols and glycols that are widely used to protect against hydrate formation and for melting hydrate plugs. Besides these two chemicals, the other common used chemical class is salts such as sodium chloride, calcium chloride and potassium formate [4].

In this experiment, application of NaCl in KHI solution was used at 0.5 wt% to compare with the inhibitor efficiency in DI water solution. Since THIs require at high dosage (10-50 wt.%) [48] will shift the equilibrium conditions of gas hydrate formation. Hence this 0.5 wt.% NaCl concentration was very low so the bulk thermodynamic properties of the fluid system will be maintained. Then it can be compared with DI water solution at the same equilibrium condition.

The comparison of results between DI water solution and 0.5 wt% NaCl are presented in Table 4.6 and Figure 4.7.

Table 4.6 Influence of NaCl added to KHIs performance.

Inhibitor	Concentration	Average T_o/T_a (^oC)	
	(ppm)	0.5% NaCl	DI water
Inhibex Bio-800	2500	2.2/2.0	2.6/-
PVCap 12k+TBAB	2500	4.3/-	5.7/4.7
PVCap 60k+TBAB	2500	5.5/4.5	7.6/6.6
Luvicap 55W	2500	6.2/5.0	6.5/5.4
PVCap 12k	2500	8.3/8.0	8.7/8.4
Vcap:VIM 1:1	2500	9.1/8.2	11.9/11.6
Vcap:VIM 9:1	2500	9.3/8.0	10.1/9.6
PVCap 8.5k	2500	9.7/8.5	9.8/8.8
PVCap 60k	2500	10.0/9.2	11.4/10.8

*****Inhibex Bio-800: kept 1 hour at 2^oC for DI water solution
kept longer at 2^oC for 0.5% NaCl

******(-) means cannot find the fast growth temperature at 2^oC with 1 hr holding time

From Table 4.6, Most of the chemicals have T_o slightly better in NaCl solution than in DI water. For example, Inhibex Bio-800 in brine solution gave a slightly lower (2.2^oC) onset temperature than in DI water solution (2.6^oC). T_a in DI water case could not be exactly defined until the 1171^{st} minute because this experiment was maintained at 2^oC only for 1 hr. On the other hand, T_a in 0.5% NaCl solution is 2^oC at the 1276^{nd} minute due to the longer holding time at 2^oC.

The T_o of chemicals in the salts solution could be prolonged longer than the chemicals in water as presented in Figure 4.7 because salts dissociate into ions which form strong coulombic attractions with water, preventing the water inclusion into the hydrate cages [15].

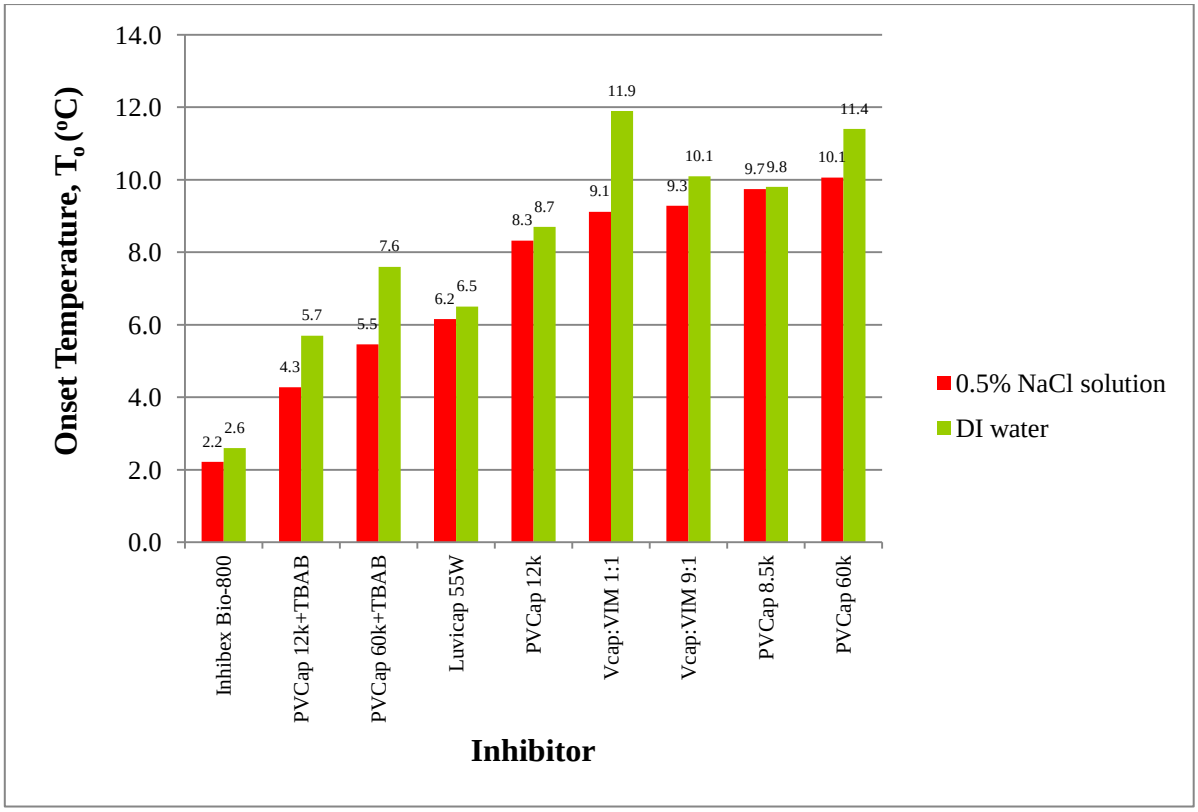


Figure 4.7 Average onset temperature for inhibitors in DI water and 0.5 wt% NaCl.

4.7 Ranking of inhibitors at 2500 ppm

The several chemicals and synergist at concentration 2500 ppm in the Table 4.7 were ranked in this experiment according to their average onset temperature. The results are given in Figure 4.8.

From the experiment, the best T_o value was Inhibex Bio-800 (PVCap copolymer in BGE). The second to the seventh chemical were Inhibex 101 (PVCap in BGE, Mw=2-5*10^3), Hybrane (Hyper-branched polyesteramides), PVCap 12k (Mw=12*10^3)+TBAB, Inhibex 501 (PVCap:VP 1:1 molar ratio in BGE, Mw=5-8*10^3), Luvicap 55W (VCap:VP copolymer 1:1)and PVCap 60k (Mw=60*10^3)+TBAB, respectively. All of the six chemicals are based on PVCap polymer except Hybrane. The reason is the inhibition mechanism of PVCap-based KHIs that are: 1) A lactam group fits vertically into an incomplete cage 2) Oxygen in the carbonyl group forms a hydrogen bonds to water molecules 3) The backbone of polymer lines between sections or on the surface of the hydrate crystal, and 4) The hydrate crystal structure is defected because large cages are unable to close [49]

According to literature, the two main classes of KHIs field applications in common commercial are based on PVCap mono-/copolymer and hyperbranched polyester amides [4]. However, these polymer themselves have limitations on the degree of subcooling, induction time and compatibility with field operating conditions [28]. Therefore, many researches develop new inhibitors with enhanced properties compared to conventional PVCap-based KHIs.

Inhibex Bio-800 and Inhibex 501 are the new synergist products. Inhibex Bio-800 gave better result in induction time and max subcooling than Inhibex 501 [28, 50]. Currently information and detail of these inhibitors are rarely published.

From PVCap-based KHIs, Inhibex 101 had lower T_o than PVCap 12k+TBAB and Inhibex 501 since the molecular weight of their chemicals as illustrated in Figure 4.8. The Mw of Inhibex 101, PVCap 12k, and Inhibex 501 are $2\text{-}5*10^3$, $12*10^3$ and $5\text{-}8*10^3$, respectively. Inhibex 101 has lower Mw than Inhibex 501, thus inhibition performance of Inhibex 101 is better. The results show that there is an optimum molecular weight that gives best performance. If molecular weight is below optimum, inhibition effect will not much because fewer interactions with hydrate surface per polymer chain. If the molecular weight increases, the number of polymer strands in solution will decrease and some of the alkylamide side chains will not available for interaction with hydrate surfaces. Therefore, high molecular weight polymers also have lower efficiency [48].

The ideal molecular weight (Mw) for the performance of a KHI polymer (or oligomer), is around 1500-3000. Performance of polymer will dramatically drop when molecular weight is below 1000. However polymer with above 3000-4000 molecular weight slowly dropping without disappearing. The advantage of low molecular weight polymer is maintaining a low viscosity of the injected formulation. Thus, samples of commercial PVCap, the highest performing currently commercial vinyl lactam polymer, have molecular weights of about 2000-4000 [4].

For PVCap 12k+TBAB and Inhibex 501, PVCap 12k+TBAB had lower T_o than Inhibex 501 although PVCap 12k had higher Mw than Inhibex 501. This is caused by TBAB. Small quaternary salts such as tetrabutylammonium bromide (TBAB) have been used as VCap polymer synergists in the field [4].

Table 4.7 KHIs performance ranking at concentration 2500 ppm

Inhibitor	Average T_o/T_a (^oC)	Inhibitor	Average T_o/T_a (^oC)
Inhibex Bio800	2.6/-	PVCap 8.5k	9.8/8.8
Inhibex 101	3.9/2.2	Inhibex 713	9.9/9.2
Hybrane	4.5/4.5	AP-1000 10k	10.0/9.3
PVCap 12k+TBAB	5.7/4.7	Vcap:Vlm_9:1	10.0/9.6
Inhibex 501	6.0/4.0	Antaron P904	10.5/9.6
Luvicap 55W	6.5/5.4	PVCap 60k	11.4/10.8
PVCap 60k+TBAB	7.6/6.6	Luvicap Bio	11.7/11.1
Paspartamide 187C	7.9/7.6	Vcap:Vlm _1:1	11.9/11.6
Luvicap EG	8.3/7.7	Agrimer 30	13.1/10.8
PNIPAM	8.5/7.9	PVP 120k	13.5/11.2
Casein Peptone Plus	8.6/8.3	Pyroglutamate	15.5/14.9
PVCap 12k	8.7/8.4	Poly Vlm	16.9/14.5
Vcap:BVIMBr_9:1	9.3/8.8	DI water	17.5/17.5

*****(-) means cannot find the fast growth temperature at 2^oC with 1 hr

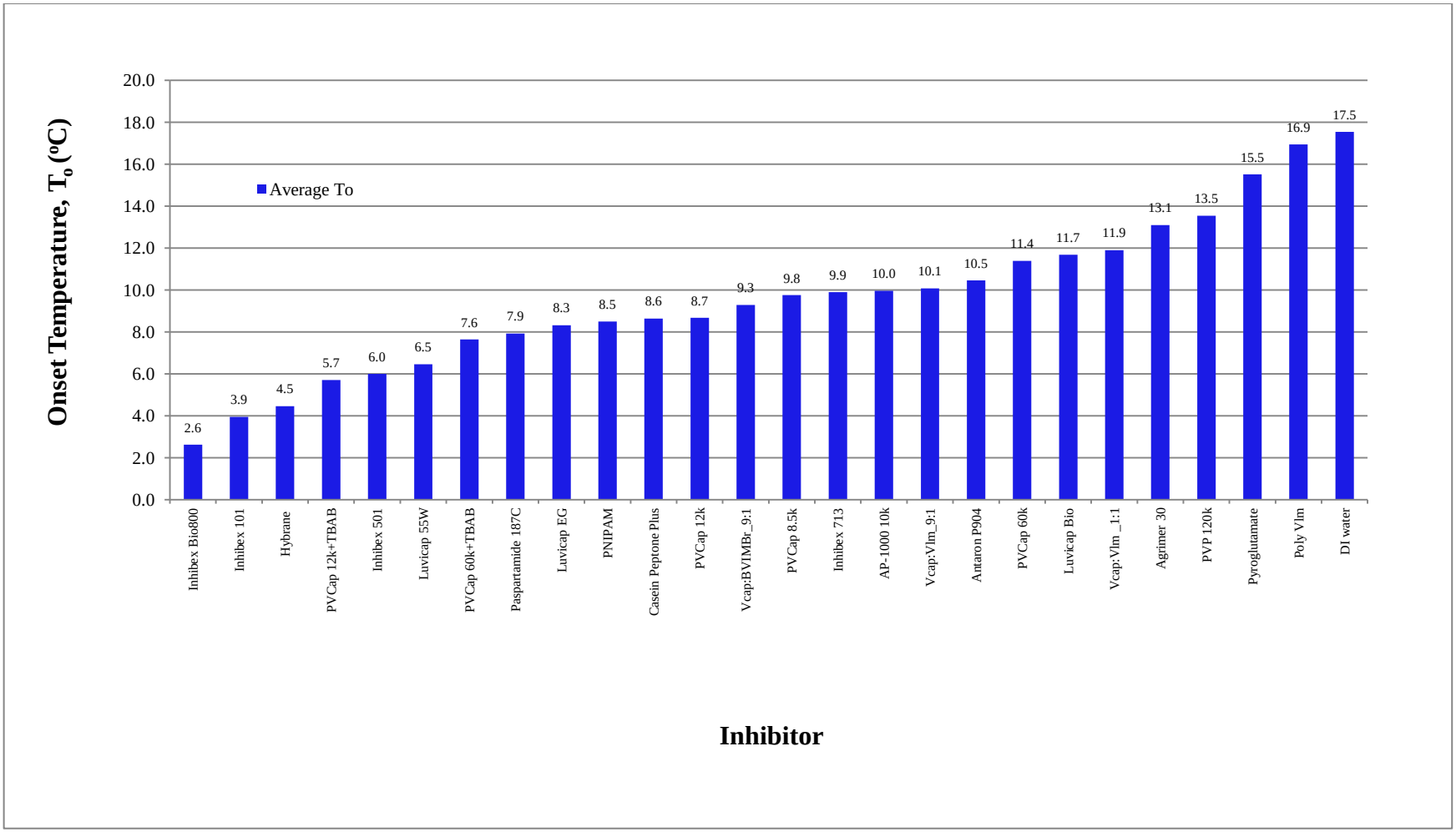


Figure 4.8 Inhibitor ranking results at concentration 2500 ppm

4.8 Ranking of inhibitors at 5000 ppm

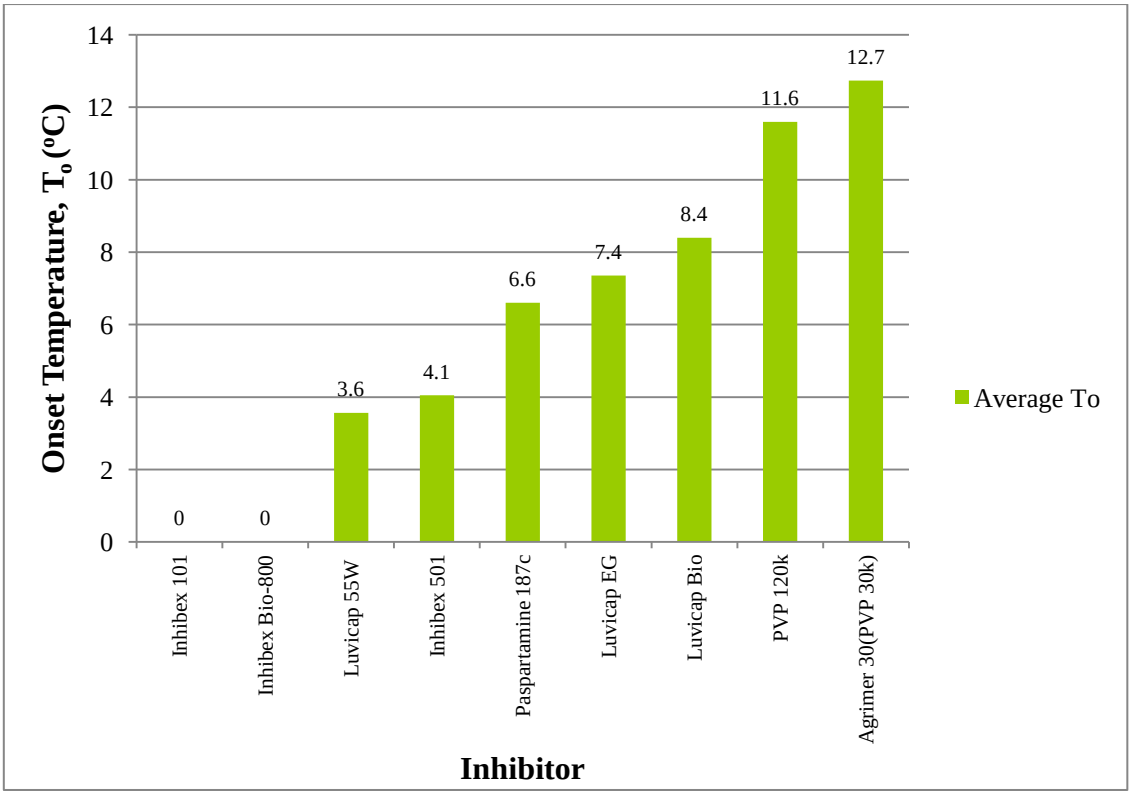
The seven chemicals with concentration 5000 ppm were ranked in the experiment as their average onset temperature. The results are given in Table 4.8 Figure 4.9.

Inhibex 101 and Inhibex Bio-800 are the best KHIs because hydrate did not form after keeping for 1 hour at 2^{o}C. Luvicap 55W and Inhibex 501 have T_o/T_a at 3.6/2.8 and 4.1/2.3 respectively. The reason is described in section 4.8. All chemicals decrease in T_o with increasing the concentrations. The explanation is in section 4.5.

Table 4.8 KHIs performance ranking at concentration 5000 ppm

Inhibitor	Average T_o/T_a (^{o}C)
Inhibex 101	0/0
Inhibex Bio-800	0/0
Luvicap 55W	3.6/2.8
Inhibex 501	4.1/2.3
Paspartamine 187c	6.6/6.6
Luvicap EG	7.4/6.5
Luvicap Bio	8.4/8.2
PVP 120k	11.6/10.1
Agrimer 30(PVP 30k)	12.7/11.0

*The cooling down method was maintained at 2^{o}C for 1 hour.



*The cooling down method was maintained at 2°C for 1 hour.

Figure 4.9 Inhibitor ranking results at concentration 5000 ppm

5 CONCLUSION

In this work, a variety of KHIs' efficiency had been tested for hydrate inhibition by using the rocking cell apparatus. The inhibition performances in term of an onset temperature are determined. The following conclusions can be drawn:

- Test results in the first few weeks may be a little worse as the new equipment is not yet "conditioned".
- The onset temperatures from a new RC5 rocking cell equipment are a little lower for the high performance inhibitors. Whereas the T_o from both RC5 units is approximately the same with low performance inhibitors.
- RC5 and autoclave cell experiments have similar T_o trends with the high performance KHIs such as Inhibex 501, Luvicap 55W and Luvicap EG. However T_o is significantly different with the low performance polymers, especially for the smallest 23ml autoclave. RC5 has a small scattering of an average T_o deviation.
- Magnets attached to the cells do not affect T_o.
- KHI performance is increased when raising KHI concentration from 2500 ppm to 5000 ppm.
- Blends of these polymers with low NaCl concentration will slightly enhance the performance beyond the thermodynamic effect of the salt.
- Regarding ranking of KHIs, it is found that Inhibex Bio800 has the lowest onset temperature follow by Inhibex 101, Hybrane, PVCap 12k+TBAB, and Inhibex 501 at 2500 ppm. Furthermore, the polymer molecular weight is shown to be critical for optimal performance.
- At 5000 ppm, Inhibex 101 and Inhibex Bio-800 are the best KHIs.

Rocking cells are prescreening equipment suitable only for ranking KHIs. To determine absolute performance of KHIs, large loops and pipe wheels are normally the last and best step to be carried out before pilot scale or field implementation [4]. Besides the performance of chemicals, there are numerous issues to be addressed in field applications such as overall cost, compatibility (cloud point, viscosity, foam, emulsions, other production chemicals etc.), and environmental impact [48].

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APPENDIX A Results of RC5 test

cooling constant method

	Temp. (°C)	time (hh:mm)
T_{start}	20.5-2	18.30
T_{low}	2	1
T_{melt}	25	1
T_{end}	20.5	0.2
Total time 20 hrs 50 mins		

volume 20 ml
rocking rate 20
rocking angle 40
steel ball

date	chemical	conc.(ppm)	To1	To2	To3	To4	To5	Av To	Ta1	Ta2	Ta3	Ta4	Ta5	Av Ta	to1	to2	to3	to4	to5	Av to	ta1	ta2	ta3	ta4	ta5	Av ta	comments
2011.11.09	DI water		18.2	19.8	18.8	18.2	18.3	**18.7**							186	89	145	166	171	**151**							to=ta and To=Ta
2012.04.04	DI water		17.1	18.0	18.1	17.3	17.2	**17.5**							205	157	154	202	213	**186**							to=ta and To=Ta
2011.11.10	Luvicap 55W	5000	4.6	4.1	4.7	5.1	4.1	**4.5**	4.1	3.4	4.3	4.6	3.8	**4.0**	1091	1101	1055	1018	1092	**1071**	1112	1121	1088	1043	1112	**1095**	
2012.01.27	Luvicap 55W	5000	3.2	3.1	4.2	3.4	3.9	**3.6**	2.4	2.5	3.2	2.6	3.3	**2.8**	1090	1094	1025	1074	1049	**1066**	1112	1107	1089	1101	1086	**1099**	
2011.12.16	Luvicap 55W	2500	6.6	6.8	6.1	6.5	7.8	**6.8**	6.3	5.7	5.0	5.8	6.5	**5.9**	879	864	910	876	797	**865**	895	930	976	923	872	**919**	
2012.04.03	Luvicap 55W	2500	5.8	7.4	6.6	6.2	6.3	**6.5**	4.9	6.6	5.3	5.2	5.2	**5.4**	930	832	884	906	900	**890**	980	881	963	967	967	**952**	
2011.12.19	Luvicap EG	2500	8.6	9.3	9.1	9.3	9.3	**9.1**	7.2	7.7	7.7	8	8	**7.7**	750	714	715	709	709	**719**	836	805	802	789	789	**804**	
2012.04.10	Luvicap EG	2500	7.9	7.8	8.3	8.7	8.9	**8.3**	7.6	7.6	7.9	7.8	7.6	**7.7**	796	796	973	737	729	**806**	814	813	797	801	808	**807**	
2011.12.20	Inhibex101	2500	5	5.1	5.4	5.4	5.1	**5.2**	2.1	2.5	2.5	3.2	2.6	**2.6**	973	971	953	950	966	**963**	1117	1108	1107	1095	1101	**1106**	
2012.04.11	Inhibex101	2500	3.8	3.8	3.9	4.1	4.1	**3.9**	2.1	2	2.1	2.5	2.1	**2.2**	1062	1055	1047	1035	1033	**1046**	1117	1118	1112	1108	1114	**1114**	
2011.12.21	Inhibex501	2500	6	7			7	**6.7**	4.3	4.8			5	**4.7**	913	855			854	**874**	1021	995			967	**994**	
2012.04.23	Inhibex501	2500	5.8	6.2	6.1	5.9	6	**6.0**	3.9	4	4	4	4	**4.0**	928	899	913	930	914	**917**	1048	1045	1039	1040	1042	**1043**	
2011.12.22	Hybrane	2500	6.4	5.7	5.8	6.5	5.5	**6.0**	6	5.4	5.4	6.2	5.2	**5.6**	900	934	933	885	942	**919**	917	947	948	901	954	**933**	
2012.04.25	Hybrane	2500	4	4.8	4.7	4.6	4.2	**4.5**	4	4.8	4.7	4.6	4.2	**4.5**	1036	982	994	1000	1024	**1007**	1036	982	994	1000	1024	**1007**	to=ta and To=Ta
2012.01.09	Pyroglutamate	2500	15.1	15.8	14.8	15.3	16.6	**15.5**	14.7	15	14.4	14.7	15.9	**14.9**	336	298	363	320	248	**313**	359	339	385	355	287	**345**	
2012.01.10	Inhibex Bio800	2500	2.5	2.4	2.6	2.6	2.8	**2.6**	not plug yet						1110	1104	1101	1099	1098	**1102**	not plug yet						not plug yet
2012.04.24	Inhibex Bio800	2500	2.7	2.5	2.5	2.6	2.8	**2.6**	not plug yet						1105	1108	1108	1108	1108	**1107**	not plug yet						not plug yet
2012.01.11	Inhibex 713	2500	9.4	9.2	10.5	10.1	10.3	**9.9**	9	8.8	9.5	9.2	9.3	**9.2**	695	706	637	664	645	**669**	725	723	693	713	696	**710**	
2012.01.12	PVP Plasdone K-12	2500	10.4	11.3	10.9	11.8	11.8	**11.2**	9.8	10.5	10.3	10.9	11	**10.5**	638	580	607	550	551	**585**	685	629	643	603	598	**632**	
2012.01.13	Agrimer 30(PVP 30k)	2500	12.6	12.2	13.4	13.5	13.8	**13.1**	10.7	10.5	11	10.7	11.3	**10.8**	495	524	448	439	418	**465**	615	630	595	613	574	**605**	
2012.01.16	PVP 120k	2500	13.3	13.9	13.2	13.8	13.5	**13.5**	10.8	11.1	11	11.6	11.6	**11.2**	456	419	460	421	444	**440**	612	592	602	565	562	**587**	
2012.01.17	Casein Peptone Plus	2500	8.8	8.8	8.3	8.9	8.4	**8.6**	8.5	8.4	8	8.4	8.1	**8.3**	739	742	766	737	763	**749**	758	762	784	760	781	**769**	window auto-restart after 896 mins
2012.01.18	PNIPAM	2500	8.5	8.5	8.5	8.6	8.4	**8.5**	7.9	7.9	8	8	7.8	**7.9**	758	756	755	752	761	**756**	792	788	785	785	802	**790**	5.44 bar leak from cell5
2012.01.19	Antaron P904	2500	10.2	10.6	10.8	10.3	10.4	**10.5**	9.5	9.6	9.7	9.5	9.6	**9.6**	650	672	621	639	642	**645**	690	689	680	689	687	**687**	
2012.01.20	Paspartamide 187C	2500	7.5	8	8	8	8.1	**7.9**	7.3	7.7	7.6	7.6	7.8	**7.6**	821	790	801	790	782	**797**	836	808	823	812	802	**816**	
2012.01.23	AP-1000 10k	2500	9.4	10.1	10	10.6	9.7	**10.0**	8.8	9.5	9.1	10	9.3	**9.3**	698	658	664	620	680	**664**	734	696	721	661	700	**702**	
2012.01.24	Luvicap 55W with magnet	2500	5.8	6.1	6.1	6	5.8	**6.0**	5	4.8	5.1	5	4.8	**4.9**	923	907	905	909	926	**914**	978	981	965	971	979	**975**	1 magnet per cell
2012.01.25	Luvicap 55W without magnet	2500	6	6.6	6.9	6.4		**6.5**	5.1	5.1	5.4	5.2		**5.2**	916	883	855	887		**885**	972	966	953	961		**963**	cell 5 leaked
2012.01.26	Luvicap 55W with magnet	2500	6.2	6.6	6.4	6.9	6.9	**6.6**	5.1	5.3	5.2	5.3	5.4	**5.3**	902	875	890	861	867	**879**	963	956	965	950	947	**956**	5 magnets at cell 1
2012.01.30	Luvicap EG	5000	7.8	7	7.2	7.4	7.4	**7.4**	6.2	6.5	6.4	6.5	6.8	**6.5**	804	851	839	826	833	**831**	897	883	886	882	864	**882**	
2012.01.31	Inhibex 101	5000	no hydrate formation																								no hydrate formation
2012.02.01	Inhibex 501	5000		3.8	3.4	4.7	4.3	**4.1**		2	2	2.7	2.6	**2.3**		1056	1080	998	1031	**1041**		1160	1137	1103	1107	**1127**	
2012.02.02	PVP 120k	5000	13.1	10.9	11.3	10.5	12.2	**11.6**	11	9.9	9.9	9.3	10.5	**10.1**	468	609	580	629	526	**562**	598	667	673	710	630	**656**	
2012.02.03	Agrimer 30(PVP 30k)	5000	13	11.8	12.3	13.8	12.8	**12.7**	10.9	10.5	11.2	11.4	10.9	**11.0**	473	556	513	425	484	**490**	611	636	581	569	606	**601**	
2012.02.06	PVP Plasdone k-12	5000	13.2	11.7	12.1	13.1	12.7	**12.6**	11.5	10.5	11.2	11.7	11.5	**11.3**	645	553	530	470	487	**537**	570	631	589	554	565	**582**	
2012.05.10	Luvicap Bio	5000	8.2	8.8	8.5	8.4	7.9	**8.4**	8	8.7	8.3	8.4	7.7	**8.2**	772	737	759	762	799	**766**	784	746	769	762	807	**774**	To=Ta, to=ta in cell 4

APPENDIX A Results of RC5 test (Continue)

cooling constant method

	Temp. (°C)	time (hh:mm)
T_{start}	20.5-2	18.30
T_{low}	2	1
T_{melt}	25	1
T_{end}	20.5	0.2
Total time 20 hrs 50 mins		

volume 20 ml
rocking rate 20
rocking angle 40
steel ball

date	chemical	conc.(ppm)	To1	To2	To3	To4	To5	Av To	Ta1	Ta2	Ta3	Ta4	Ta5	Av Ta	to1	to2	to3	to4	to5	Av to	ta1	ta2	ta3	ta4	ta5	Av ta	comments
2012.02.07	Luvicap Bio	2500	11.9	11.5	11.3	12.3	11.4	**11.7**	11.3	10.9	10.9	11.5	11	**11.1**	547	577	589	515	582	**562**	582	608	609	567	602	**594**	
2012.02.08	Inhibex Bio-800	5000	no hydrate formation																								no hydrate formation
2012.02.15	PVCap 12k	2500	8.4	8.4	9.4	8.7	9.5		8.1	8.2	9.1	8.5	9.1		760	762	699	743	695		774	775	718	755	714		
2012.02.23	PVCap 12k	2500	8.5	8.2	8.7	8.3	8.6	**8.7**	8.2	7.9	8.4	8	8.4	**8.4**	754	769	742	767	741	**743**	769	788	759	786	754	**759**	
2012.02.16	PVCap 60k	2500	11.1	11	11.1	11.5	11.3		10.5	10.5	10.6	10.8	10.6		594	600	604	571	585		630	628	627	609	624		
2012.02.24	PVCap 60k	2500	11.8	11.6	11.5	11.5	11.5	**11.4**	11	10.9	10.8	11	10.9	**10.8**	545	567	567	571	570	**577**	593	610	616	606	604	**615**	
2012.03.12	PVCap 8.5k	2500	10.1	9.8	9.3	10	9.4		8.4	8.7	8.7	9.3	8.8		653	674	701	668	694		762	736	737	711	729		
2012.03.19	PVCap 8.5k	2500	10.5	10.5	9.3	9.3	9.3	**9.8**	8.6	8.7	8.9	8.9	8.9	**8.8**	630	632	709	706	701	**677**	748	746	734	734	730	**737**	
2012.03.13	Vcap:BVIMBr_9:1	2500	9.6	9.4	9.6	9.7	8.3		9.2	9	9.1	9.1	8.2		690	698	683	683	772		715	728	713	717	783		
2012.03.20	Vcap:BVIMBr_9:1	2500	9.6	10.6	9.1	8.7	8.3	**9.3**	9.1	9	8.6	8.4	8.2	**8.8**	693	630	726	751	771	**710**	724	729	750	766	778	**740**	
	Vcap:Vlm _1:1	2500	11.8	11.9	11	11.6	13.1	**11.9**	11.4	11.6	10.8	11.3	12.8	**11.6**													retest
2012.03.15	Vcap:Vlm_9:1	2500	9.6	9.4	10.8	10.9	9.5		9.3	9	10	10	9.2		679	689	618	609	695		704	715	664	657	708		
2012.03.26	Vcap:Vlm_9:1	2500	9.7	10.4	10.5	10.1	9.8	**10.1**	9.3	9.7	10	9.5	9.5	**9.6**	680	634	634	660	675	**657**	697	676	665	690	688	**686**	
2012.03.16	Poly Vlm	2500	16.3	16.8	16.7	17.4	17		13.9	13.9	14.6	14.6	14.3		261	237	237	200	220		412	420	377	380	391		
2012.03.27	Poly Vlm	2500	17.4	16.9	17.6	16.7	16.6	**16.9**	14.2	14.2	15.3	14.7	15.6	**14.5**	201	219	186	244	250	**226**	397	394	333	367	313	**378**	
2012.03.22	PVCap 60k+TBAB	2500	7.3	7.8	8	7.9	7.8		6.5	6.6	6.8	7	6.7		834	815	799	800	811		887	871	859	853	870		
2012.03.29	PVCap 60k+TBAB	2500	8	8.5	8	5.8	7.3	**7.6**	6.8	6.9	6.9	4.6	6.8	**6.6**	792	762	787	928	838	**817**	860	855	853	1002	863	**877**	
2012.03.23	PVCap 12k+TBAB	2500	6	5.9	6.3	6.4	6.6		4.4	4.8	4.8	4.9	4.9		923	920	895	888	873		1013	988	987	980	980		
2012.03.30	PVCap 12k+TBAB	2500	5.3	6	4.6	5	4.9	**5.7**	4.6	4.7	4.4	4.6	4.7	**4.7**	956	914	1006	972	977	**932**	1004	998	1018	999	997	**996**	
2012.04.26	PVCap 60k_NaCl	2500	10.4	9.8	10	10.1	10	**10.1**	9.3	9	9.2	9.2	9.3	**9.2**	633	676	662	656	659	**657**	708	722	710	711	708	**712**	in 0.5% NaCl solution
2012.04.27	PVCap 12k_NaCl	2500	8.4	9	8	8.2	8	**8.3**	8	8.7	7.7	7.9	7.7	**8.0**	760	728	784	775	789	**767**	784	751	805	793	808	**788**	in 0.5% NaCl solution
2012.04.30	PVCap 8.5k_NaCl	2500	10.2	9.5	9.6	9.8	9.6	**9.7**	8.2	8.7	8.7	8.5	8.3	**8.5**	654	701	690	676	687	**682**	774	752	748	758	768	**760**	in 0.5% NaCl solution
2012.05.02	Luvicap 55W_NaCl	2500	6.2	6.2	6.3	6.5	5.6	**6.2**	4.7	4.8	5.3	5.3	4.8	**5.0**	905	899	896	879	939	**904**	996	988	959	952	989	**977**	in 0.5% NaCl solution
2012.05.03	VCap_Vlm 9_1_NaCl	2500	9	9.4	9.4	9.5	9.1	**9.3**	7.9	8	8.1	8.2	8	**8.0**	721	702	707	696	716	**708**	794	790	787	784	789	**789**	in 0.5% NaCl solution
2012.05.04	VCap BVIMBr_NaCl	2500	7.8	7.2	8.1	7.8	8.8	**7.9**	7.4	6.9	7.7	7.5	8.2	**7.5**	808	842	783	803	741	**795**	828	858	813	822	777	**820**	in 0.5% NaCl solution
2012.05.07	VCap_Vlm 1:1_NaCl	2500	8.7	9.1	9.1	9.4	9.3		7.8	8.1	8.1	8.2	8.2		742	720	721	705	711	**720**	796	782	781	778	778	**783**	in 0.5% NaCl solution
	VCap_Vlm 1:1_NaCl	2500	8.7	9.4	9	9.3	8.9	**9.1**	8.3	8.6	8.4	8.6	8.1	**8.2**													retest
2012.05.08	PVCap 60k+TBAB_NaCl	2500	5.3	5.5	5.5	5.5	5.5	**5.5**	4.2	4.3	4.7	4.9	4.6	**4.5**	957	946	947	948	945	**949**	1029	1015	998	984	1006	**1006**	in 0.5% NaCl solution
2012.05.09	PVCap 12k+TBAB_NaCl	2500	4.5	4.1	4.7	4.3	3.8	**4.3**	not plug yet						1005	1031	991	1016	1057	**1020**	not plug yet						in 0.5% NaCl solution
2012.05.11	Inhibex Bio-800_NaCl	2500	2.3	2.4	2	2.4	2	**2.2**	2	2	2	2	2	**2.0**	1110	1108	1121	1105	1147	**1118**	1314	1204	1302	1217	1343	**1276**	**48 hrs at 2oC**

APPENDIX B Results of autoclave test

Cell 1	Autoclave cell (200ml)
Cell 2	Autoclave cell (23ml)
Conditions	constant cooling from 20.5°C to 2°C in 18,5 hours
	600 rpm

		Cell 1												Cell 2											
chemical	**conc.(ppm)**	**To1**	**To2**	**To3**	**To4**	**To5**	**Av To**	**Ta1**	**Ta2**	**Ta3**	**Ta4**	**Ta5**	**Av Ta**	**To1**	**To2**	**To3**	**To4**	**To5**	**Av To**	**Ta1**	**Ta2**	**Ta3**	**Ta4**	**Ta5**	**Av Ta**	**comments**
DI water	2500	13.3					**13.3**	13.3					**13.3**	11.2					**11.2**	11.2					**11.2**	
Luvicap 55W	2500	6.6	6.6	6.8	6.55	6.6	**6.63**	5.8	5.9	6.28	5.83	6	**5.962**	6.6	6.9	6.6			**6.7**	6	6.3	6.2			**6.2**	
Luvicap EG	2500	6.9	7.85	8.35	6.1	8.05	**7.45**	6.5	7.3	7.6	5.5	6.6	**6.7**	8					**8**	7.3					**7.3**	
PVP Plasdone k-12	2500	8.3	10.9	11.09	11.3	10.9	**10.498**	7.9	10.4	10.5	10.8	10.5	**10.02**	7.85	10.95	11.1			**10.0**	7.5	10.5	10.6			**9.5**	
Agrimer 30(PVP 30k)	2500	11.55	12.15	12.4	11.6	12.05	**11.95**	10.65	11.1	11.25	10.6	10.9	**10.9**	12.45	10.9	11.4	12.7	10	**11.49**	6	6.6	6.65	7.6	6.7	**6.71**	
Inhibex 501	2500	6.6	6.2	5.8	6.4	6.2	**6.24**	5	4.85	4.6	4.7	5.1	**4.85**	5.9	6	4.1	6	4.9	**5.38**	4.4	3.2	3.1	3.7		**3.6**	

APPENDIX C Percentage deviation from average of T_o and T_a

cooling constant method

	Temp. (°C)	time (hh:mm)
T_{start}	20.5-2	18.30
T_{low}	2	1
T_{melt}	25	1
T_{end}	20.5	0.2
Total time 20 hrs 50 mins		

volume 20 ml
rocking rate 20
rocking angle 40
steel ball

DV=Deviation

date	chemical	conc.(ppm)	To1	To2	To3	To4	To5	Av To	Ta1	Ta2	Ta3	Ta4	Ta5	Av Ta	comments	To1	To2	To3	To4	To5	Ta1	Ta2	Ta3	Ta4	Ta5
2011.11.09	DI water		18.2	19.8	18.8	18.2	18.3	**18.66**							to=ta and To=Ta	2.47	-6.11	-0.75	2.47	1.93					
2012.04.04	DI water		17.1	18.0	18.1	17.3	17.2	**17.54**							to=ta and To=Ta	2.51	-2.62	-3.19	1.37	1.94					
2011.11.10	Luvicap 55W	5000	4.6	4.1	4.7	5.1	4.1	**4.52**	4.1	3.4	4.3	4.6	3.8	**4.04**		-1.77	9.29	-3.98	-12.83	9.29	-1.49	15.84	-6.44	-13.86	5.94
2012.01.27	Luvicap 55W	5000	3.2	3.1	4.2	3.4	3.9	**3.56**	2.4	2.5	3.2	2.6	3.3	**2.80**		10.11	12.92	-17.98	4.49	-9.55	14.29	10.71	-14.29	7.14	-17.86
2011.12.16	Luvicap 55W	2500	6.6	6.8	6.1	6.5	7.8	**6.76**	6.3	5.7	5.0	5.8	6.5	**5.86**		2.37	-0.59	9.76	3.85	-15.38	-7.51	2.73	14.68	1.02	-10.92
2012.04.03	Luvicap 55W	2500	5.8	7.4	6.6	6.2	6.3	**6.46**	4.9	6.6	5.3	5.2	5.2	**5.44**		10.22	-14.55	-2.17	4.02	2.48	9.93	-21.32	2.57	4.41	4.41
2011.12.19	Luvicap EG	2500	8.6	9.3	9.1	9.3	9.3	**9.12**	7.2	7.7	7.7	8	8	**7.72**		5.70	-1.97	0.22	-1.97	-1.97	6.74	0.26	0.26	-3.63	-3.63
2012.04.10	Luvicap EG	2500	7.9	7.8	8.3	8.7	8.9	**8.32**	7.6	7.6	7.9	7.8	7.6	**7.70**		5.05	6.25	0.24	-4.57	-6.97	1.30	1.30	-2.60	-1.30	1.30
2011.12.20	Inhibex101	2500	5	5.1	5.4	5.4	5.1	**5.20**	2.1	2.5	2.5	3.2	2.6	**2.58**		3.85	1.92	-3.85	-3.85	1.92	18.60	3.10	3.10	-24.03	-0.78
2012.04.11	Inhibex101	2500	3.8	3.8	3.9	4.1	4.1	**3.94**	2.1	2	2.1	2.5	2.1	**2.16**		3.55	3.55	1.02	-4.06	-4.06	2.78	7.41	2.78	-15.74	2.78
2011.12.21	Inhibex501	2500	6	7			7	**6.67**	4.3	4.8			5	**4.70**		10.00	-5.00			-5.00	8.51	-2.13			-6.38
2012.04.23	Inhibex501	2500	5.8	6.2	6.1	5.9	6	**6.00**	3.9	4	4	4	4	**3.98**		3.33	-3.33	-1.67	1.67	0.00	2.01	-0.50	-0.50	-0.50	-0.50
2011.12.22	Hybrane	2500	6.4	5.7	5.8	6.5	5.5	**5.98**	6	5.4	5.4	6.2	5.2	**5.64**		-7.02	4.68	3.01	-8.70	8.03	-6.38	4.26	4.26	-9.93	7.80
2012.04.25	Hybrane	2500	4	4.8	4.7	4.6	4.2	**4.46**	4	4.8	4.7	4.6	4.2	**4.46**	to=ta and To=Ta	10.31	-7.62	-5.38	-3.14	5.83	10.31	-7.62	-5.38	-3.14	5.83
2012.01.09	Pyroglutamate	2500	15.1	15.8	14.8	15.3	16.6	**15.52**	14.7	15	14.4	14.7	15.9	**14.94**		2.71	-1.80	4.64	1.42	-6.96	1.61	-0.40	3.61	1.61	-6.43
2012.01.10	Inhibex Bio800	2500	2.5	2.4	2.6	2.6	2.8	**2.58**	not plug yet						not plug yet	3.10	6.98	-0.78	-0.78	-8.53					
2012.04.24	Inhibex Bio800	2500	2.7	2.5	2.5	2.6	2.8	**2.62**	not plug yet						not plug yet	-3.05	4.58	4.58	0.76	-6.87					
2012.01.11	Inhibex 713	2500	9.4	9.2	10.5	10.1	10.3	**9.90**	9	8.8	9.5	9.2	9.3	**9.16**		5.05	7.07	-6.06	-2.02	-4.04	1.75	3.93	-3.71	-0.44	-1.53
2012.01.12	PVP Plasdone K-12	2500	10.4	11.3	10.9	11.8	11.8	**11.24**	9.8	10.5	10.3	10.9	11	**10.50**		7.47	-0.53	3.02	-4.98	-4.98	6.67	0.00	1.90	-3.81	-4.76
2012.01.13	Agrimer 30(PVP 30k)	2500	12.6	12.2	13.4	13.5	13.8	**13.10**	10.7	10.5	11	10.7	11.3	**10.84**		3.82	6.87	-2.29	-3.05	-5.34	1.29	3.14	-1.48	1.29	-4.24
2012.01.16	PVP 120k	2500	13.3	13.9	13.2	13.8	13.5	**13.54**	10.8	11.1	11	11.6	11.6	**11.22**		1.77	-2.66	2.51	-1.92	0.30	3.74	1.07	1.96	-3.39	-3.39
2012.01.17	Casein Peptone Plus	2500	8.8	8.8	8.3	8.9	8.4	**8.64**	8.5	8.4	8	8.4	8.1	**8.28**	window auto-restart after 896 mins	-1.85	-1.85	3.94	-3.01	2.78	-2.66	-1.45	3.38	-1.45	2.17
2012.01.18	PNIPAM	2500	8.5	8.5	8.5	8.6	8.4	**8.50**	7.9	7.9	8	8	7.8	**7.92**	5.44 bar leak from cell5	0.00	0.00	0.00	-1.18	1.18	0.25	0.25	-1.01	-1.01	1.52
2012.01.19	Antaron P904	2500	10.2	10.6	10.8	10.3	10.4	**10.46**	9.5	9.6	9.7	9.5	9.6	**9.58**		2.49	-1.34	-3.25	1.53	0.57	0.84	-0.21	-1.25	0.84	-0.21
2012.01.20	Paspartamide 187C	2500	7.5	8	8	8	8.1	**7.92**	7.3	7.7	7.6	7.6	7.8	**7.60**		5.30	-1.01	-1.01	-1.01	-2.27	3.95	-1.32	0.00	0.00	-2.63
2012.01.23	AP-1000 10k	2500	9.4	10.1	10	10.6	9.7	**9.96**	8.8	9.5	9.1	10	9.3	**9.34**		5.62	-1.41	-0.40	-6.43	2.61	5.78	-1.71	2.57	-7.07	0.43
2012.01.24	Luvicap 55W with magnet	2500	5.8	6.1	6.1	6	5.8	**5.96**	5	4.8	5.1	5	4.8	**4.94**	1 magnet per cell	2.68	-2.35	-2.35	-0.67	2.68	-1.21	2.83	-3.24	-1.21	2.83
2012.01.25	Luvicap 55W without magnet	2500	6	6.6	6.9	6.4		**6.48**	5.1	5.1	5.4	5.2		**5.20**	cell 5 leaked	7.34	-1.93	-6.56	1.16		1.92	1.92	-3.85	0.00	
2012.01.26	Luvicap 55W with magnet	2500	6.2	6.6	6.4	6.9	6.9	**6.60**	5.1	5.3	5.2	5.3	5.4	**5.26**	5 magnets at cell 1	6.06	0.00	3.03	-4.55	-4.55	3.04	-0.76	1.14	-0.76	-2.66
2012.01.30	Luvicap EG	5000	7.8	7	7.2	7.4	7.4	**7.36**	6.2	6.5	6.4	6.5	6.8	**6.48**		-5.98	4.89	2.17	-0.54	-0.54	4.32	-0.31	1.23	-0.31	-4.94
2012.01.31	Inhibex 101	5000	no hydrate formation												no hydrate formation										
2012.02.01	Inhibex 501	5000		3.8	3.4	4.7	4.3	**4.05**		2	2	2.7	2.6	**2.33**			6.17	16.05	-16.05	-6.17		13.98	13.98	-16.13	-11.83
2012.02.02	PVP 120k	5000	13.1	10.9	11.3	10.5	12.2	**11.60**	11	9.9	9.9	9.3	10.5	**10.12**		-12.93	6.03	2.59	9.48	-5.17	-8.70	2.17	2.17	8.10	-3.75
2012.02.03	Agrimer 30(PVP 30k)	5000	13	11.8	12.3	13.8	12.8	**12.74**	10.9	10.5	11.2	11.4	10.9	**10.98**		-2.04	7.38	3.45	-8.32	-0.47	0.73	4.37	-2.00	-3.83	0.73
2012.02.06	PVP Plasdone k-12	5000	13.2	11.7	12.1	13.1	12.7	**12.56**	11.5	10.5	11.2	11.7	11.5	**11.28**		-5.10	6.85	3.66	-4.30	-1.11	-1.95	6.91	0.71	-3.72	-1.95
2012.05.10	Luvicap Bio	5000	8.2	8.8	8.5	8.4	7.9	**8.36**	8	8.7	8.3	8.4	7.7	**8.22**	To=Ta, to=ta in cell 4	1.91	-5.26	-1.67	-0.48	5.50	2.68	-5.84	-0.97	-2.19	6.33

APPENDIX C Percentage deviation from average of T_o and T_a (Continue)

cooling constant method

	Temp. (°C)	time (hh:mm)
T_{start}	20.5-2	18.30
T_{low}	2	1
T_{melt}	25	1
T_{end}	20.5	0.2
Total time 20 hrs 50 mins		

volume 20 ml
rocking rate 20
rocking angle 40
steel ball

DV=Deviation

date	chemical	conc.(ppm)	To1	To2	To3	To4	To5	Av To	Ta1	Ta2	Ta3	Ta4	Ta5	Av Ta	comments	To1	To2	To3	To4	To5	Ta1	Ta2	Ta3	Ta4	Ta5
2012.02.07	Luvicap Bio	2500	11.9	11.5	11.3	12.3	11.4	**11.68**	11.3	10.9	10.9	11.5	11	**11.12**		-1.88	1.54	3.25	-5.31	2.40	-1.62	1.98	1.98	-3.42	1.08
2012.02.08	Inhibex Bio-800	5000	no hydrate formation												no hydrate formation										
2012.02.15	PVCap 12k	2500	8.4	8.4	9.4	8.7	9.5		8.1	8.2	9.1	8.5	9.1			3.11	3.11	-8.42	-0.35	-9.57	3.46	2.26	-8.46	-1.31	-8.46
2012.02.23	PVCap 12k	2500	8.5	8.2	8.7	8.3	8.6	**8.67**	8.2	7.9	8.4	8	8.4	**8.39**		1.96	5.42	-0.35	4.27	0.81	2.26	5.84	-0.12	4.65	-0.12
2012.02.16	PVCap 60k	2500	11.1	11	11.1	11.5	11.3		10.5	10.5	10.6	10.8	10.6			2.55	3.42	2.55	-0.97	0.79	2.42	2.42	1.49	-0.37	1.49
2012.02.24	PVCap 60k	2500	11.8	11.6	11.5	11.5	11.5	**11.39**	11	10.9	10.8	11	10.9	**10.76**		-3.60	-1.84	-0.97	-0.97	-0.97	-2.23	-1.30	-0.37	-2.23	-1.30
2012.03.12	PVCap 8.5k	2500	10.1	9.8	9.3	10	9.4		8.4	8.7	8.7	9.3	8.8			-3.59	-0.51	4.62	-2.56	3.59	4.44	1.02	1.02	-5.80	-0.11
2012.03.19	PVCap 8.5k	2500	10.5	10.5	9.3	9.3	9.3	**9.75**	8.6	8.7	8.9	8.9	8.9	**8.79**		-7.69	-7.69	4.62	4.62	4.62	2.16	1.02	-1.25	-1.25	-1.25
2012.03.13	Vcap:BVIMBr_9:1	2500	9.6	9.4	9.6	9.7	8.3		9.2	9	9.1	9.1	8.2			-3.34	-1.18	-3.34	-4.41	10.66	-4.66	-2.39	-3.53	-3.53	6.71
2012.03.20	Vcap:BVIMBr_9:1	2500	9.6	10.6	9.1	8.7	8.3	**9.29**	9.1	9	8.6	8.4	8.2	**8.79**		-3.34	-14.10	2.05	6.35	10.66	-3.53	-2.39	2.16	4.44	6.71
	Vcap:Vlm _1:1	2500	11.8	11.9	11	11.6	13.1	**11.9**	11.4	11.6	10.8	11.3	12.8	**11.6**	retest	0.67	-0.17	7.41	2.36	-10.27	1.55	-0.17	6.74	2.42	-10.54
2012.03.15	Vcap:Vlm_9:1	2500	9.6	9.4	10.8	10.9	9.5		9.3	9	10	10	9.2			4.67	6.65	-7.25	-8.24	5.66	2.62	5.76	-4.71	-4.71	3.66
2012.03.26	Vcap:Vlm_9:1	2500	9.7	10.4	10.5	10.1	9.8	**10.07**	9.3	9.7	10	9.5	9.5	**9.55**		3.67	-3.28	-4.27	-0.30	2.68	2.62	-1.57	-4.71	0.52	0.52
2012.03.16	Poly Vlm	2500	16.3	16.8	16.7	17.4	17		13.9	13.9	14.6	14.6	14.3			3.78	0.83	1.42	-2.72	-0.35	4.34	4.34	-0.48	-0.48	1.58
2012.03.27	Poly Vlm	2500	17.4	16.9	17.6	16.7	16.6	**16.94**	14.2	14.2	15.3	14.7	15.6	**14.53**		-2.72	0.24	-3.90	1.42	2.01	2.27	2.27	-5.30	-1.17	-7.36
2012.03.22	PVCap 60k+TBAB	2500	7.3	7.8	8	7.9	7.8		6.5	6.6	6.8	7	6.7			4.45	-2.09	-4.71	-3.40	-2.09	0.91	-0.61	-3.66	-6.71	-2.13
2012.03.29	PVCap 60k+TBAB	2500	8	8.5	8	5.8	7.3	**7.64**	6.8	6.9	6.9	4.6	6.8	**6.56**		-4.71	-11.26	-4.71	24.08	4.45	-3.66	-5.18	-5.18	29.88	-3.66
2012.03.23	PVCap 12k+TBAB	2500	6	5.9	6.3	6.4	6.6		4.4	4.8	4.8	4.9	4.9			-5.26	-3.51	-10.53	-12.28	-15.79	5.98	-2.56	-2.56	-4.70	-4.70
2012.03.30	PVCap 12k+TBAB	2500	5.3	6	4.6	5	4.9	**5.70**	4.6	4.7	4.4	4.6	4.7	**4.68**		7.02	-5.26	19.30	12.28	14.04	1.71	-0.43	5.98	1.71	-0.43
2012.04.26	PVCap 60k_NaCl	2500	10.4	9.8	10	10.1	10	**10.06**	9.3	9	9.2	9.2	9.3	**9.20**	in 0.5% NaCl solution	-3.38	2.58	0.60	-0.40	0.60	-1.09	2.17	0.00	0.00	-1.09
2012.04.27	PVCap 12k_NaCl	2500	8.4	9	8	8.2	8	**8.32**	8	8.7	7.7	7.9	7.7	**8.00**	in 0.5% NaCl solution	-0.96	-8.17	3.85	1.44	3.85	0.00	-8.75	3.75	1.25	3.75
2012.04.30	PVCap 8.5k_NaCl	2500	10.2	9.5	9.6	9.8	9.6	**9.74**	8.2	8.7	8.7	8.5	8.3	**8.48**	in 0.5% NaCl solution	-4.72	2.46	1.44	-0.62	1.44	3.30	-2.59	-2.59	-0.24	2.12
2012.05.02	Luvicap 55W_NaCl	2500	6.2	6.2	6.3	6.5	5.6	**6.16**	4.7	4.8	5.3	5.3	4.8	**4.98**	in 0.5% NaCl solution	-0.65	-0.65	-2.27	-5.52	9.09	5.62	3.61	-6.43	-6.43	3.61
2012.05.03	VCap_Vlm 9_1_NaCl	2500	9	9.4	9.4	9.5	9.1	**9.28**	7.9	8	8.1	8.2	8	**8.04**	in 0.5% NaCl solution	3.02	-1.29	-1.29	-2.37	1.94	1.74	0.50	-0.75	-1.99	0.50
2012.05.04	VCap BVIMBr_NaCl	2500	7.8	7.2	8.1	7.8	8.8	**7.94**	7.4	6.9	7.7	7.5	8.2	**7.54**	in 0.5% NaCl solution	1.76	9.32	-2.02	1.76	-10.83	1.86	8.49	-2.12	0.53	-8.75
2012.05.07	VCap_Vlm 1:1_NaCl	2500	8.7	9.1	9.1	9.4	9.3		7.8	8.1	8.1	8.2	8.2		in 0.5% NaCl solution	4.29	-0.11	-0.11	-3.41	-2.31	5.34	1.70	1.70	0.49	0.49
	VCap_Vlm 1:1_NaCl	2500	8.7	9.4	9	9.3	8.9	**9.1**	8.3	8.6	8.4	8.6	8.1	**8.2**	retest	4.29	-3.41	0.99	-2.31	2.09	-0.73	-4.37	-1.94	-4.37	1.70
2012.05.08	PVCap 60k+TBAB_NaCl	2500	5.3	5.5	5.5	5.5	5.5	**5.46**	4.2	4.3	4.7	4.9	4.6	**4.54**	in 0.5% NaCl solution	2.93	-0.73	-0.73	-0.73	-0.73	7.49	5.29	-3.52	-7.93	-1.32
2012.05.09	PVCap 12k+TBAB_NaCl	2500	4.5	4.1	4.7	4.3	3.8	**4.28**	not plug yet						in 0.5% NaCl solution	-5.14	4.21	-9.81	-0.47	11.21					
2012.05.11	Inhibex Bio-800_NaCl	2500	2.3	2.4	2	2.4	2	**2.22**	2	2	2	2	2	**2.00**	**48 hrs at 2oC**	-3.60	-8.11	9.91	-8.11	9.91	0.00	0.00	0.00	0.00	0.00

APPENDIX D Abbreviation

LDHIs	Low Dosage Hydrate Inhibitors
KHIs	Kinetic Hydrate Inhibitors
AAs	Anti-agglomerant
SI	Structure I
CSI	Cubic structure I
SII	Structure II
CSII	Cubic structure II
SH	Structure H
HSIII	Hexagonal structure H
THIs	Thermodynamic Hydrate Inhibitors
MEG	Monoethylene glycol
DEG	Diethylene glycol
TEG	Triethylene glycol
HSE	Health, Safety and Environment
CAPEX	Capital Expenditure
OPEX	Operational Expenditure
VP	N-vinylpyrrolidone
PVP	Polyvinylpyrrolidone
PVCap	Polyvinylcaprolactam
CI	Corrosion Inhibitor
VIMA	N-methyl-N-vinylacetamide
VCAP	Vinylcaprolactam
GHI1	Polyvinylpyrrolidone and diethylene glycol monobutylether in the weight ratio 1:1
THF	Tetrahydrofuran
NaCl	Sodium chloride
Mw	The weight average molecular weight
BGE	monobutyl glycol ether
DMAEMA	dimethylaminoethyl methacrylate
PNIPAM	poly(N-isopropylacrylamide)
TBAB	tetrabutylammonium bromide

VIM	Vinylimmidazole
AP	Acryloylpyrrolidine
ΔT	Subcooling
T_o	The onset temperature
T_a	The temperature of catastrophic growth process
t_o	The onset time
t_a	The time of catastrophic growth process
t_i	Induction time