Synergistic Performance of Pectin with Monoethylene glycol as Environment Friendly and Sustainable Hydrate Inhibitor

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ABSTRACT

This research explores the capability of pectin as a hydrate inhibitor, along with its potential synergy with monoethylene glycol (MEG). The inhibitory performance was evaluated by measuring the induction time (IT) required for hydrate formation under various concentrations (0.25 wt%, 0.5 wt%, and 1 wt%), employing methane gas at a pressure of 7.6 MPa with hydrate equilibrium temperature at 10.45 °C. The cooling process was meticulously maintained at a consistent rate of 1°C per hour below the hydrate equilibrium temperature throughout the experiment. Results revealed that while pectin exhibited slightly lower performance compared to commercial Kinetic Hydrate Inhibitors (KHIs), it demonstrates promising potential as a viable alternative to traditional non-biodegradable and unsustainable KHIs. However, when blended with MEG, its performance increased rapidly. This is particularly significant for the smooth operation of the oil and gas industry offshore, where environmental concerns take precedence. The ability of pectin and MEG combination to effectively inhibit hydrate formation, combined with their biodegradable properties, positions it as an attractive candidate for future research in the field of deep-sea hydrate risk management.

Keywords: Oil and gas; Hydrate blockages; Kinetic hydrate inhibitors; Pectin monoethylene glycol; Biodegradable.

1. INTRODUCTION

Oil and gas transmission must be unhindered for the industry to operate effectively. Offshore flowlines often operate in situations where temperatures and pressures are favorable for hydrate development; as a result, they are vulnerable to blockage from hydrate formation (Mahmoud *et al.* 2014). Hydrate plugs are dangerous to the pipeline and may cause pipeline rupture causing economical and financial harm, therefore hydrate inhibition is essential for efficient working of the oil and gas industry. Figure 1 depicts a hydrate plug formed during one of our experiments.

The industry typically injects methanol or glycol for hydrate inhibition (Anderson and Prausnitz 1986), which are also referred to as thermodynamic hydrate inhibitors (THIs). When added to the production stream, THIs change the hydrate equilibrium to higher pressure and colder temperatures. However, for effective hydration inhibition(Wu *et al.* 2007), a sizable quantity of THI (10 - 40 wt%) is typically needed to significantly lower the equilibrium temperature. Purchasing, transporting and storing huge amount of THIs is quite expensive (Chin and Srivastava, 2018). They are also very flammable and toxic. Benign kinetic hydrate inhibitors (KHIs) are promising alternatives for

minimizing the cost of THIs, reducing large quantity requirements and to address environmental concerns. Over the past two decades, KHIs, typically polymers derived and developed from crude oil petrochemical fractions soluble in water, have been developed, tested, and deployed by the industry (Fu *et al.* 2001; Frostman *et al.* 2003; Glénat *et al.* 2004; Swanson *et al.* 2005; Wang *et al.* 2013). Typically, KHIs delay the formation of hydrates and slow down the crystal growth of hydrates (Carver *et al.* 1995; O'Reilly *et al.* 2011) via different proposed inhibition mechanisms such as hydrogen bonding between the KHI and the water molecules, not allowing the water molecules to form stable nucleation crystals. However, none of these mechanisms are well understood and modeled due to the complexity of the molecular interactions.

MacDonald *et al.* (2006) have reported three field applications of KHIs in hydrate inhibition. The first application is in an Offshore UK Sector where a standard 24-inch flow line connects three gas platforms. The 69 km long flowline faces 4-8 °C subcooling (hydrate equilibrium temperature minus the minimum operating temperature). Earlier, a combination of two THIs, triethylene glycol (TEG) and MEG, was used to inhibit hydrate formation. However, there have been frequent shutdowns due to MEG/TEG regeneration, machine's

failures to dehydrate the gas and several trip requirements to fix the units and to remove the hydrate obstructions. In 1997 a KHI product was introduced into the system, and since then, no new hydrate formation issues have been documented. Over $3 million in cost savings are realized in the first year of operation by the operator due to the usage of KHI.

Fig. 1. Methane hydrate plug

In the second application, a 17 km subsea pipeline connected an autonomous platform to an onshore terminal. Comparatively, a low subcooling of 1-5°C is faced in this case. A KHI was used for hydrate inhibition, and not a single event of plugging due to hydrate was reported until the end of the field life. Five production wells are part of an onshore system in the third field application by MacDonald. The system also has water reinjection wells, but because the gas and water aren't separated prior to injection, hydrates occasionally form in the water injection lines. Depending on the weather, the system faces a subcooling of 7–13°C. A KHI product was suggested by the researchers for the specific conditions, and no hydrate formation was observed in the injection lines since then, which has saved the operator several thousand dollars. Although the majority of KHIs are not toxic (Gad *et al.* 1987; Fu *et al.* 2002; Exon 2006), they are not biodegradable (Magnusson et al. 2018). Numerous incidents involving the inability of polymer KHIs to degrade hydrate plugs have been documented (Exon 2006; Eubeler *et al.* 2009; Eubeler *et al.* 2010; Lin *et al.* 2017; Farhadian *et al.* 2019). Hence, KHIs are prohibited in several places worldwide due to non-biodegradability (Kelland, 2018). This requires the hydrate inhibitor chemistry towards developing biodegradable and environment-friendly and sustainable inhibitor products (Singh and Suri, 2020; Singh and Suri, 2021; Singh and Suri, 2022; Singh *et al.* 2023b; Singh and Suri, 2023; Singh *et al.* 2023a).

Therefore, in the present study, the hydrate inhibiting potential of pectin is evaluated. Pectin is an inherent polysaccharide that naturally occurs and can be found within the cellular structures of various plants. It is commonly obtained through the extraction process from the rinds and pulp of apple and citrus fruits for commercial purposes(Colin, 1990). The molecular configuration of pectin is illustrated in Fig. 2. It comprises a multitude of saccharide units, primarily composed of galacturonic acid, interspersed with some methyl esters, forming a chain-like arrangement. Its molecular weight typically falls within the range 50,000 to 150,000 gram/mole (Dorota *et al.* 2003). Pectin possesses excellent biodegradability, demonstrating more than 90 % degradation within a 28-day period according to the OECD 306 test (Pereira *et al.* 2021). Additionally, it has been established as non-toxic. Furthermore, pectin exhibits natural prophylactic properties, effectively safeguarding against heavy metal poisoning, such as lead and mercury (Rudolf, 1982). Notably, pectin can also delay the formation of hydrates due to the hydroxyl groups found in its side chains, which have the capacity to form hydrogen bonds with water molecules, thereby retarding the process of hydrate formation (Xu *et al.* 2016; Yaqub *et al.* 2019; Yaqub *et al.* 2021).
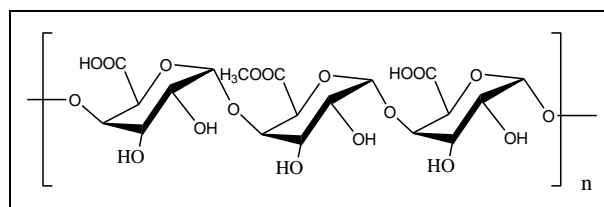

Fig. 2: Molecular structure of pectin

2. METHODOLOGY

Standard constant cooling rate tests were carried out in an autoclave to form methane hydrates and to examine the hydration-inhibiting effectiveness of individual and synergistic mixtures of pectin with MEG. The induction time was computed from the experimental data.

2.1 Material and Source

All chemicals tested were obtained from TCI chemicals.

2.2 Apparatus Used

An autoclave at high pressure with cooling capacity and SCADA system was used in all the tests, as shown in Fig. 3. The equipment details were covered in depth in our earlier work (Singh and Suri 2022b). In

summary, the cell volume is 0.5 L that can be pressurized up to 200 bars and cooled down to -10 °C at different constant cooling rate such as, 1 °C/hour. Gas-water

mixture stirring at a variable rate was provided using a magnetic stirrer up to a stirring speed of 1000 rpm.
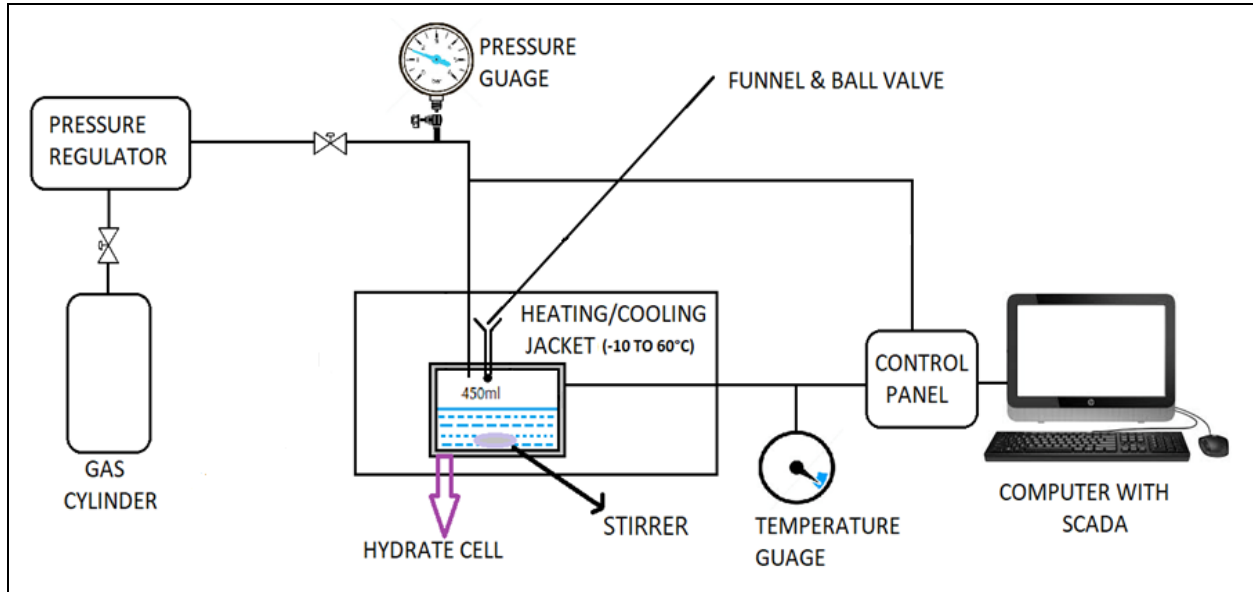

Fig. 3: Diagram of the autoclave setup (Singh and Suri, 2022b) for hydrate formation and inhibitor performance evaluation

2.3 Experimental Procedure

Hydrate formation and inhibitor testing was done using a constant cooling rate procedure (Singh and Suri, 2020; 2021). The detailed constant cooling experimental process can be accessed from our previous work (Singh and Suri, 2022). Figure 4 illustrates a standard plot depicting the recorded test parameters, including temperature, pressure, and time, during a consistent cooling experiment. In each experimental trial, we combine 150 mL of distilled water with varying concentrations of pectin and industrial hydrate inhibitors to create distinct blend ratios. For a distilled water-methane system at 7.6 MPa the hydrate equilibrium temperature (T_{eq}) is equal to 10.45 °C as found from CSM-Gem (Colorado school of Mines Gibbs Energy Minimization) research free software.

First, the cell was filled with distilled water and the temperature was reduced to the hydrate equilibrium temperature. Pure methane was introduced and pressure was increased to 7.6 MPa. The cell was then sealed, and a stirrer was used to stir the distilled water methane mixture at a speed of 600 rpm. Once the pressure and stirring were stabilized, cooling at a constant rate of 1°C/hour was applied. Pressure and temperature readings with time were recorded by SCADA until at least 0 °C is reached. Gradual temperature reduction causes pressure to reduce until hydrate formation. However, a sudden

pressure reduction is observed at hydrate nucleation temperature due to the entrapment of free-pressured gas in the hydrate crystals. The time taken for hydrate formation from the equilibrium temperature is termed as induction time (IT) which is calculated from equation 1.
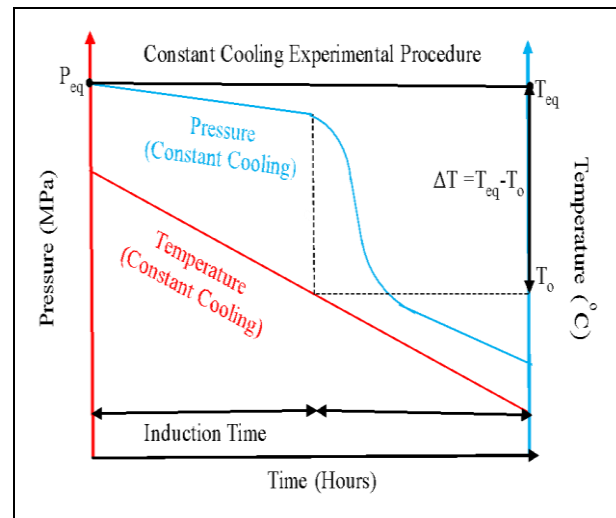

Fig. 4: General pressure and temperature curves during constant cooling hydrate formation/inhibition experiments

$$Change\ in\ induction\ time\ (\%)$$
$$= \frac{IT_{(blend)} - IT_{(Pure\ KHI)}}{IT_{(Pure\ KHI)}}$$
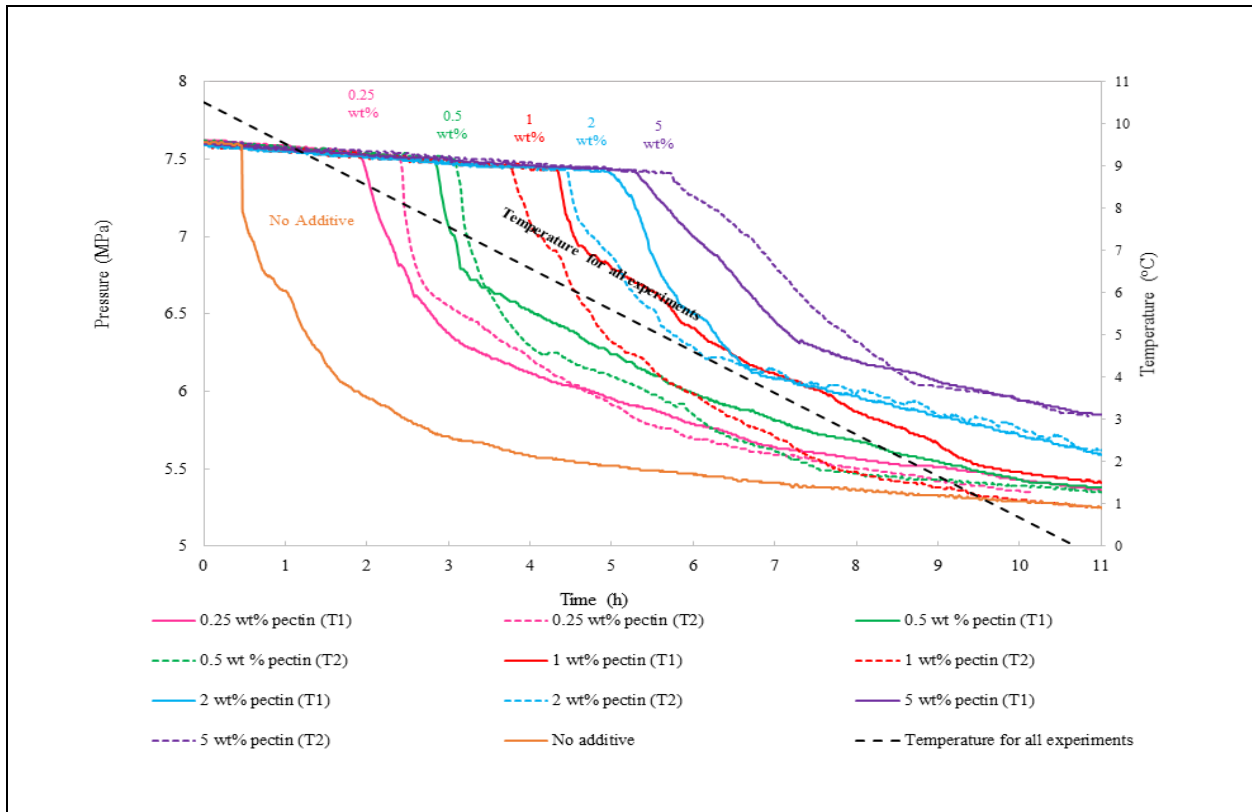$$* 100 \qquad ……………… (1)$$

Fig. 5: General pressure and temperature curves during constant cooling hydrate formation/inhibition

Temperature data is averaged in the plots for clarity as it is almost the same for each experiment.

Table 1. Induction time details for pectin at different concentrations

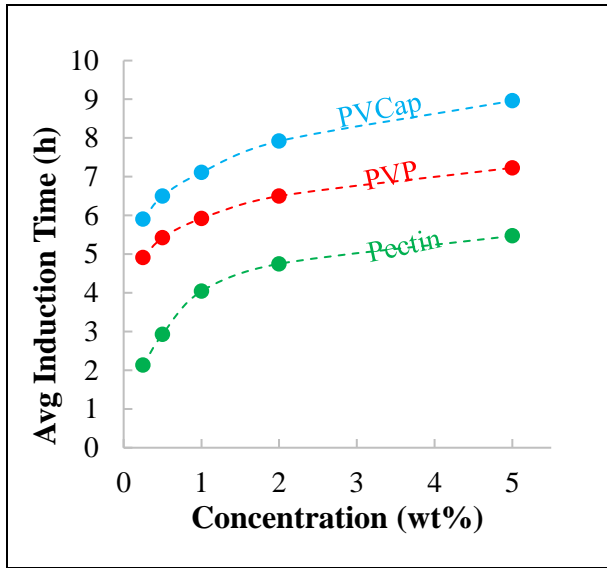| E. No.	KHI	Conc (wt%)	T_{eq} (°C)	Test No.	T_o (°C)	IT (h)	Avg IT (h)	IT std dev (h)
1		0 2 5		T-1	8.54	1.91	2.13	0.30
2				T-2	8.11	2.34		
3		0 5		T-1	7.63	2.82	2.92	0.15
4				T-2	7.42	3.03		
5	Pectin	1	10.45	T-1	6.11	4.34	4.04	0.42
6				T-2	6.71	3.74		
7		2		T-1	5.40	5.05	4.75	0.41
8				T-2	6	4.45		
9		5		T-1	4.71	5.74	5.47	0.38
10				T-2	5.25	5.2		

Fig. 6: Comparison of the average Induction Times (IT) for pectin, polyvinyl pyrrolidone (PVP) and poly(N-vinylcaprolactam (PVCap) at different concentrations (Singh and Suri, 2022a; Singh *et al.* 2023c)

3. RESULTS AND DISCUSSION

3.1 KHI Performance of Pectin

Experiments were performed at 0.25, 0.5, 1, 2 and 5 wt% of pectin for performance benchmarking.

Experimental results measured for each of the individual inhibitors are presented in Fig. 5. It was observed that upon increasing the concentration of the different inhibitors, there was an increase in the IT.

From Fig. 6, it can be observed that performance of pectin is slightly slower than commercial KHI. It still demonstrates promising potential as a viable alternative to traditional non-biodegradable and unsustainable KHIs.

3.2 KHI performance of pectin - MEG blends

After obtaining the results for pectin as a standalone kinetic hydrate inhibitor, the groundwork was laid for investigating the potential synergy in hydrate inhibition between MEG and pectin. To explore this synergy, four distinct concentrations of MEG ranging from 0.5 % to 20 % by weight were combined with 0.25 % pectin for testing purposes. Figure 7 depicts the outcomes of two separate sets of hydrate formation experiments, showcasing the variations in pressure and temperature over time. The repeated tests are indicated by solid and dashed lines of the same color. Table 2 provides a summary of the results, including the hydrate nucleation temperature (To) and induction times (ITs) for both sets of experiments, along with their corresponding averages and standard deviations.
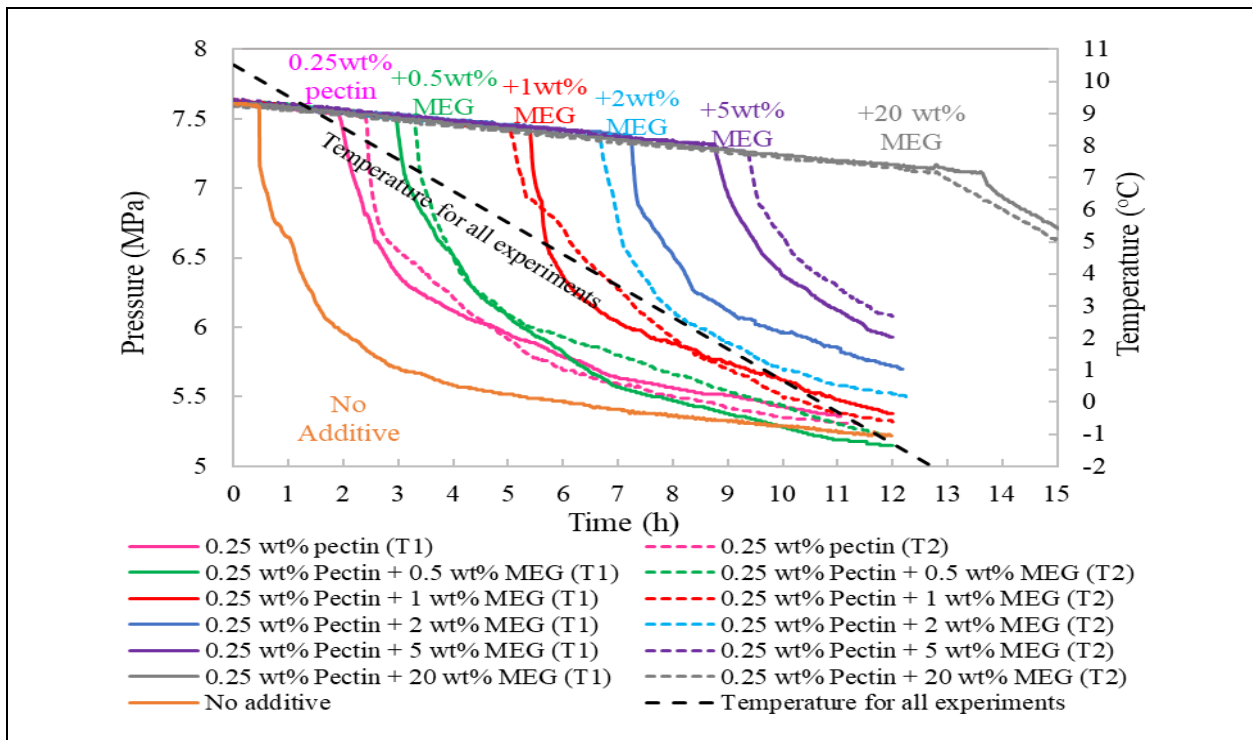

Fig. 7: Hydrate formation results for pectin blended MEG

Table 2. Average To and IT values for pectin MEG blends

S. No.	KHI	Conc of MEG (wt %)	Blend T_{eq} (°C)	Test No.	Blend T_o (°C)	Average T_o (°C)	Blend IT (h)	Average IT (h)	IT (h) std dev
1	Pectin (0.25 wt%)	0	10.45	T-1	8.54	8.32	1.91	2.13	0.30
2				T-2	8.11		2.34		
3		0.5	10.35	T-1	7.52	7.33	2.83	3.02	0.26
4				T-2	7.15		3.2		
5		1	10.24	T-1	5.06	5.25	5.18	4.98	0.28
6				T-2	5.45		4.79		
7		2	10.03	T-1	3.20	3.50	6.83	6.53	0.42
8				T-2	3.80		6.23		
9		5	9.38	T-1	1.71	1.39	7.67	7.99	0.45
10				T-2	1.08		8.3		
11		20	4.95	T-1	-3.19	-2.83	8.14	7.78	0.49
12				T-2	-2.47		7.42		

Table 2 shows the influence of varying MEG concentrations with a pectin solution of 0.25 wt% on the average temperature at which hydrate inhibition occurs (IT). When the mixture includes 0.5 wt% MEG along with 0.25 wt% pectin, it results in a reduction of the average temperature at which hydrate formation begins (To) to 7.33°C, subsequently resulting in an average IT of 3.02 hours. Likewise, increasing the MEG concentration to 1 wt% leads to a decrease in the average To to 5.25°C, thereby elevating the average IT to 4.98 hours. When 2 wt% MEG is combined with 0.25 wt% pectin, the average temperature for hydrate formation stabilizes at approximately 3.5°C, leading to an average IT of 6.53 hours. Furthermore, when 5 wt% MEG is mixed with 0.25 wt% pectin, the To diminishes to 1.39°C, resulting in an IT of 7.99 hours. Finally, introducing 20 wt% MEG to 0.25 wt% pectin exhibits a significant reduction in nucleation temperature (-2.83). However, the resulting IT remains almost unchanged when compared to the scenario with 5 wt% MEG. Hence, it can be concluded that increasing the concentration of MEG solvent beyond 5 wt% does not substantially enhance the IT of pectin.
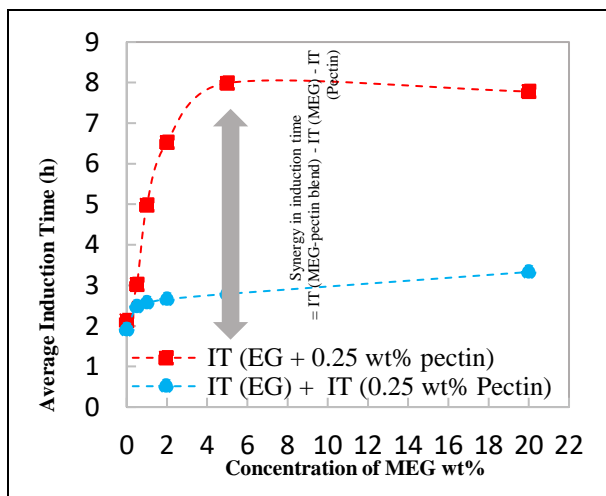
Figure 8 illustrates both the blend ITs and the cumulative ITs of separate MEG and pectin components. The presence of synergy between the chemicals for hydrate inhibition can be determined by comparing the blend IT with the sum of individual ITs. The figure reveals that synergy levels are relatively low when MEG constitutes less than 0.5 wt% of the blend, but they rise significantly as MEG concentration increases, reaching a peak at 5 wt%. Subsequently, there is a slight reduction in synergy, although it remains substantial.

4. CONCLUSIONS

From our experiments, we observed that pectin exhibited slightly lower performance compared to commercial kinetic hydrate inhibitors. Yet, it holds significant promise as a viable alternative to traditional non-biodegradable and unsustainable options, especially in offshore locations where environmental considerations take precedence. Additionally, when pectin is combined with MEG, it acts as a synergistic agent, enhancing its hydrate inhibition performance as the MEG concentration increases, up to 5 wt%. Beyond this concentration, increasing the MEG content decreases the overall hydrate nucleation temperature (To). However, the kinetic hydrate inhibition performance reaches a plateau after reaching 5 wt% MEG. The combined capability of the pectin and MEG blend to inhibit hydrate formation, along with their biodegradable nature, positions them as attractive candidates for further research in the realm of deep-sea hydrate risk management.

ACKNOWLEDGEMENT

Fig. 8. Synergistic hydrate inhibition by the pectin-MEG blends

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CONFLICT OF INTEREST

Authors have no conflict of interest.

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