The Impact of Ethylene Glycol on Droplet Growth Inhibition in Ethylene Vinyl Acetate Emulsions

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ABSTRACT: Pour point depressant (PPD) emulsion has been gaining attention in crude oil transportation owing to its potential to solve solidification issues that arise in cold climate environments. An emulsion system provides a wide range of temperature application that combines good shelf life and tunable thermal properties to tackle this problem. These features can be achieved by incorporating an antifreeze agent into the emulsion. One of the most commonly used antifreeze agents is ethylene glycol (EG).

Hence, this study focuses on the thermal properties and droplet size growth of PPD emulsions that were aged in variable concentrations of EG solution. EG50 exhibited the lowest freezing temperature of $-44^\circ$C, while EG25 demonstrated the lowest vitrification temperature of $-68.7^\circ$C. The particle size of the emulsions underwent a significant reduction from 332.3 to 228.9 nm upon the stepwise EG concentration increment to EG50. However, when the concentration was increased to EG75, a slight increase in the emulsion particle size was observed with a recorded value of 237.8 nm. Thus, it is concluded that EG50 represents the optimum concentration for delivering the best freezing protection and producing a smaller droplet particle size.

INTRODUCTION

The transportation of crude oil via pipelines is becoming more challenging because of the drop in temperature in pipelines. Crude oil is a complex mixture of hydrocarbons and comprises waxes, resins, saturates, asphaltenes, naphthenics, dissolved gases, water, and salts. Among all these substances, waxes, which in this case refer to paraffin wax, have become the major hindrance in the transporting of crude oil. This is because paraffin wax tends to precipitate in cold environments and sticks on the walls of pipelines, which in turn causes serious problems in the crude oil transportation. This situation will adversely impact the overall pipeline operation by decreasing the production rates, increasing the power requirements, and causing failure of facilities.

Therefore, the addition of chemical additives has been seen as a more feasible alternative in solving the wax precipitation issue owing to its more economical nature. Among the available additives, pour point depressant (PPD) is the most commonly used additive to solve this problem. To date, numerous PPD polymers have been formulated for wax inhibition process. For example, ethylene vinyl acetate (EVA) copolymer is one of the most commercially utilized PPDs.

Normally, a solvent-based PPD is used in the chemical treatment of paraffin wax. However, PPD solidification tends to occur in the solvent-based PPD when operated in a subambient climate. This consequently leads to complication since the PPD needs to be primarily heated before injecting into pipelines. Thus, PPD emulsion has been selected to improve the PPD adaptability in different oilfield climate temperatures. PPD emulsion offers better physical handling properties compared to the solvent-based PPD as well as avoiding the solidification of PPD in the injection line. Ding et al. had pinpointed that the application of emulsion as a delivery system in fish oil had enhanced its physical handling properties. An emulsion often consists of two immiscible liquids that co-exist in one temporary phase, where usually one of the liquids will be dispersed as droplets into the other. However, the major drawback of an emulsion is its thermally unstable quality, which makes it easily affected by climate change. Properties such as phase stability and crystallization temperature depend largely on the composition of the emulsion itself. In order to achieve the highest efficiency, an emulsion must remain as a liquid at low temperatures, particularly when it involves the application of $-10^\circ$C or lower temperatures.
A freezing phenomenon could reduce the shelf life of an emulsion and causes issues during certain applications especially those that require the emulsion to be constantly in liquid form at low temperatures. During freezing, phase transition occurs in an emulsion medium and causes the continuous phase to crystallize first, which later induces a destabilization mechanism. This happens due to the extensive volume expansion of the medium during freezing, which exerts pressure on the droplets and push them toward each other, causing collision. Ding et al. have also emphasized in their study that temperature posed a significant impact on the gelatin droplet behavior when subjected to low temperatures as compared to a fresh sample.

An antifreeze agent is defined as an additive that, when added into a water-based fluid, will reduce the freezing point of the mixture. It provides basic protections against freezing, boiling-over, and corrosion. Ethylene glycol (EG) has been extensively used as an antifreeze agent due to its effectiveness in reducing the freezing point of aqueous-based fluids. By incorporating an antifreeze agent into a PPD emulsion, the freezing point of the mixture can be reduced significantly. Nasir et al. reported in their study that the incorporation of EG in EVA emulsions provides the best droplet protection against temperature change and also displays good antifreezing

Figure 1. DSC thermograms of (a) cooling and (b) heating cycles of EVA emulsions with different ethylene glycol contents.
properties. Several studies have been conducted to observe the capability of EVA emulsions in providing good flowability and stability for sub-ambient applications. For instance, Umoruddin et al. pinpointed that the stability and flow response of EVA emulsions at low temperatures were influenced by the surfactant system implemented in the formulation.

Thus far, no further studies regarding the impacts of EG concentration in the EVA PPD emulsion toward the emulsion formation and freezing properties are reported. It is crucial to prevent any separation during the temperature change. Jennings and Newberry underlined that a PPD emulsion that requires to be applied in sub-ambient temperatures must have superior stability and ideal thermal properties as to prevent any blockage in the injection line. Thus, it is necessary to determine the optimum EG concentration needed to achieve the finest protection against cold climates without sacrificing the standard stability properties of the emulsion. In this study, a series of PPD emulsions with different EG concentrations were developed. The effect of EG concentration on the stability of EVA emulsions during the freeze–thaw cycle and isothermal storage was investigated. Additionally, the impacts of EG concentration toward the freezing temperature and particle size distribution of the emulsions were also addressed through this study.

### RESULTS AND DISCUSSION

A set of five EVA emulsion samples with different ethylene glycol (EG) contents was prepared and tested via DSC in order to assess their thermal behaviors in a low temperature environment. Figure 1 illustrates the DSC thermograms of cooling and heating cycles of the emulsion samples prepared with variable EG contents of 0, 25, 50, and 75 wt %. Nonetheless, the thermogram for the EVA-EG system with 100 wt % EG is unavailable since the emulsion failed to remain stable and had to be separated after several hours of preparation (Figure 3). Based on a simple test conducted to investigate the phase separation issue in the 100 wt % EG system (Table 1), it was found that the separation was caused by the insolvability of the surfactant in the system. This leads to functionality failure in the surfactant, thus causing separation in the emulsion in such a short period of time. Therefore, the EVA-EG emulsion with 100 wt % EG content was not included in the characterization study, stability evaluation, and performance testing as the results may not reflect the intended research objectives.

In reference to Figure 1 and Table 2, it can be seen that the melting points of the emulsions decreased from 5.5 °C to −44 °C with increasing EG content. This effectively proves the theory that a higher antifreeze agent content will lower the freezing point of an emulsion system. The devitrification temperature however was only present for EG25 and EG50 (−69.7 and −58.7 °C, respectively) as no crystallization peaks (refer to Figure 1(a)) were observed for the remaining emulsion samples upon heating (or re-warming). Several irregularities were also observed via the DSC thermograms obtained from this particular study as follows: (a) the non-existence of peaks for both cooling and heating thermograms of the EG75 emulsion system, (b) the absence of devitrification temperature for the EG00 EVA emulsion system, and (c) the presence of both crystallization and devitrification peaks for the EG25 EVA emulsion system.

Foremost, for the EVA emulsion with 75 wt % EG content, both melting and devitrification temperatures were not present. Two possible reasons for this occurrence are the temperature range being too narrow and the complete vitrification of the liquid. It is also possible for both reasons to coincide in light of the fact that the crystallization and devitrification temperatures of the 75 wt % EG–water mixture reached beyond −100 °C. As a result, no crystallization was observed during the testing. With an absence of ice crystals in the emulsion, it is logically conclusive that melting point is not reached as there is no ice to melt during the heating process.

Subsequently, by observing the heating thermogram of the EG00 EVA emulsion system, no devitrification peaks were present. This is because no EG was present in the system to inhibit the formation of ice nuclei. Thus, the emulsion tends to behave like water upon cooling. On the other hand, sharp peaks were noticed in the cooling and heating thermograms of the EG00 EVA emulsion system (around −20 and 5.5 °C, respectively) corresponding to crystallization and melting of ice, respectively. Thus, it can be concluded that these behaviors are expected to occur when a pure water system is used as a continuous phase.

As for the EG25 EVA emulsion system, both crystallization and devitrification peaks were present in the obtained DSC thermograms. The presence of a crystallization peak at 25 wt % EG demonstrates that the emulsion could only resist ice nucleation (crystallization or freezing) up to approximately −95 °C and melts around −12.5 °C. The small devitrification peaks present however demonstrate the possible incomplete inhibition of some ice nuclei, which therefore were inhibited during the heating of the emulsion. This shows that the EG25 EVA emulsion system does possess a vitrification ability, albeit only moderately.

### Table 1. Time Taken for the Surfactant to Dissolve inside the Medium of EVA Emulsions

| temperature (°C) | ethylene glycol concentration (%) |
|------------------|----------------------------------|
| 0                | soluble                          |
| 25               | soluble                          |
| 50               | soluble                          |
| 75               | soluble                          |
| 100              | insoluble                         |

Insoluble: produces cloudy solutions after 1 hour of stirring and form separate

*The pictures provided show the state of the solution after being left standing at room temperature for 24 h.*

### Table 2. Melting Point and Devitrification Temperature of EVA Emulsions with Different Ethylene Glycol Contents as Obtained from DSC Thermogram Analysis

| EG content (wt %) | melting point (°C) | devitrification temperature, T_d (°C) |
|-------------------|-------------------|--------------------------------------|
| 0                 | 5.5               | N/A                                  |
| 25                | −12.5             | −68.7                                |
| 50                | −44.0             | −58.7                                |
| 75                | −                 | −                                    |
| 100               | N/A               | N/A                                  |

*N/A, not applicable.*
The EG75 EVA emulsion demonstrated the best performance in terms of lowering the freezing point of the emulsion system owing to the fact that it did not freeze at all but vitrified instead. However, considering the cost factor, the EG50 EVA emulsion system is much more preferred on account of the lower usage of EG and its excellent vitrification efficiency. Moreover, it also did not crystallize upon cooling, and the freezing point considerably fell within the range of application.

The mean particle size of the EVA emulsions with different EG contents was measured, and the results are displayed in Figure 2 and Table 3, representing the particle size distribution and mean particle size, respectively. From the observation, an increment in the EG content up to 50 wt % has proven to decrease the droplet size originally from 332.3 to 228.9 nm. However, when the content of EG was further increased to 75 wt %, the mean particle size displayed a slight increase to 237.8 nm. Besides that, the distribution of size had shifted toward the right, indicating the presence of larger-sized droplets in the system.

Reflecting back to the results presented in Table 1 on the solubility of the surfactant in five different sets of the EG system, it is observable that the EG75 solution consumed the longest set of time to dissolve the surfactant. This is due to the low amount of water present in the system necessary for stimulating the surfactant. This fact is supported by the result demonstrated by the 100 wt % EG solution, where the surfactant was completely undissolved. In addition, the low amount of water also limits the effectiveness of the surfactant, in which it reduces the ability of the oil droplets to repel each other. Thus, due to this effect, the EVA emulsion was rapidly destabilized in a matter of overnight (Figure 3). Umoruddin et al.\textsuperscript{27} demonstrated that the solubility of the surfactant plays a significant impact on the EVA emulsion, which eventually impairs the emulsion flowability even with the presence of EG as an antifreeze agent.

Thus, from the aspect of particle size, it can be concluded that the EG50 EVA emulsion system provided the optimum result, whereby a minimum amount of EG was required in order to obtain the lowest particle size value and distribution. This also minimizes the particle size growth due to the effects of storage of the product, which may lead to several breakdown mechanisms in emulsions such as coalescence, Ostwald ripening, and flocculation.\textsuperscript{32}

![Figure 2. Particle size distribution of EVA emulsions of different ethylene glycol (EG) contents: 0, 25, 50, and 75 wt %.

![Figure 3. EVA emulsion with 100 wt % content of ethylene glycol after being left at room temperature overnight. The emulsion creaming occurred during the storage process due to the insolubility of the surfactant used inside a system of 100% EG.](https://dx.doi.org/10.1021/acsomega.0c01114)
underwent isothermal storage. A study by Ding et al., which spotted when feature conditions, revealed that a coalescence behavior was evaluated the changes of droplet size under various temperature−was stored at °C. This clarified the importance of antifreeze agent incorporation in preventing the coalescence process and the droplet size increment. The distribution curves illustrated in Figure 5 also confirmed the gain in the particle size by the slight shift in the distribution curves to the right as a result of the freeze−thaw cycle. Rosdi et al. emphasized that a proper freezing protection is required to prevent coalescence among interconnected frozen droplets upon heating during a freeze−thaw testing. An improper protection could lead to the formation of bigger-sized droplets as demonstrated by the right shift in the particle size distribution curve. However, in general, it can be concluded that the EG50 EVA emulsion system is the most preferred system compared to the others as it provided the smallest particle size value. This finding is in agreement with the results of DSC analysis presented in Figure 1, where the thermal properties of the emulsions affected their capability to remain stable during the freeze−thaw cycle. The selection of a suitable EG content for an EVA emulsion application in a cold climate environment is dependent on several criteria: (a) ability to provide adequate freezing protection and lowers the freezing point of an emulsion to a considerable level and (b) ability to produce the smallest possible particle size in order to minimize the effect of droplet growth during the storage period.

Thus, from this study, in order to further optimize the performance of EVA emulsions in cold climate applications, it has been concluded that the EG50 system is the most suitable system for EVA emulsions. This is because the EG50 EVA emulsion system demonstrated the smallest droplet particle size of 228.9 nm and decent thermal properties (−44 °C freezing temperature). These achieved properties comply with the stringent requirement for sub-ambient temperature applications, wherein an emulsion must remain stable in the fluid state at all temperature conditions as to secure the injection line from any blockage. The EG75 system was indeed superior in terms of freezing protection as it displayed no crystallization during cooling. However, the excessive usage of EG limits its application due to the higher operating cost compared to the EG50 system.

In order to investigate the effect of different antifreeze dosages on the performance of EVA emulsions in lowering the pour point of crude oil, a test of pour point was conducted according to the ASTM D97 method using five sets of dosages of 250, 500, 750, 1000, and 1250 ppm. The test results are discussed in this section. In general, an optimal performance was observed for all samples at 1000 ppm. The pour point reductions for EG00, EG25, EG50, and EG75 at this dosage were 5, 7, and 6 °C, respectively. Beyond this dosage, the performance of the PPD samples started to decline even with the increment of dosage. This manifestation is referred to as the pour point reversion.

Figure 4 presents the data on the particle size analysis of EVA emulsions with different EG contents acquired during the isothermal storage for a 1 week period. From the obtained results, it can be seen that there is an increment in particle size throughout the week, although the growth of the droplets was not really noteworthy. This is due to the very small differences between the droplet sizes, which were approximately in the average of 0.02 μm. The EVA-EG system in general had provided the most resistance toward droplet growth during the isothermal storage with either very little or no increment in terms of particle size for a progression of 3 weeks. Similarly, Nasir et al. stated that EVA emulsions incorporated with EG demonstrated an insignificant increment in droplet size as compared to propylene glycol and glycerol incorporation.

According to Figure 4, the graph portrays the comparison of particle size between the samples that underwent freeze−thaw cycle and the fresh samples plus the 1 week aged samples. Overall, it can be seen that the repeated freeze−thaw cycle had indeed affected the particle size of the emulsions whereby the highest increment was displayed compared to those that underwent isothermal storage. A study by Ding et al., which evaluated the changes of droplet size under various temperature conditions, revealed that a coalescence behavior was spotted when fish-oil emulsion (without any antifreeze agent) was stored at °C. This clarifies the importance of antifreeze agent incorporation in preventing the coalescence process and the droplet size increment. The distribution curves illustrated in Figure 5 also confirmed the gain in the particle size by the slight shift in the distribution curves to the right as a result of the freeze−thaw cycle. Rosdi et al. emphasized that a proper freezing protection is required to prevent coalescence among interconnected frozen droplets upon heating during a freeze−thaw testing. An improper protection could lead to the formation of bigger-sized droplets as demonstrated by the right shift in the particle size distribution curve. However, in general, it can be concluded that the EG50 EVA emulsion system is the most preferred system compared to the others as it provided the smallest particle size value. This finding is in agreement with the results of DSC analysis presented in Figure 1, where the thermal properties of the emulsions affected their capability to remain stable during the freeze−thaw cycle. The selection of a suitable EG content for an EVA emulsion application in a cold climate environment is dependent on several criteria: (a) ability to provide adequate freezing protection and lowers the freezing point of an emulsion to a considerable level and (b) ability to produce the smallest possible particle size in order to minimize the effect of droplet growth during the storage period.

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From the trend displayed in Figure 6, it can be seen that the different EG contents imposed in each emulsion insignificantly affected the pour point reduction of the wax solution. Again, this is due to the fact that the same polymer type was used in all emulsions, as stated by Yang et al.\textsuperscript{10} The pour point reduction of a PPD emulsion is dependent on the type of polymer that is being used. Thus, the variation in the antifreeze agent content in an emulsion plays no significant part with regard to the emulsion performance itself.

**CONCLUSIONS**

The selection of an optimal EG concentration in an EVA emulsion system is proven to be critical in order to enable its application in cold climates. EG is capable of improving the EVA emulsion thermal behavior and stability by eliminating the volume expansion of water, which consequently leads to neighboring droplet collision, hence inhibiting the droplet growth. The thermal analysis on all EVA emulsions (excluding EG100 EVA) revealed that the EG addition had substantially lowered the freezing point of the EVA emulsions. The EG75 EVA emulsion displayed the best performance in terms of lowering the freezing point. However, in view of the cost factor, the EG50 EVA emulsion system proved to be the most optimal system. Even at a lower EG concentration, EG50 EVA exhibited an exceptional vitrification efficiency with acceptable freezing point of within the range of application. The particle size distribution implied that any further increment of EG concentration than optimum did not dramatically change the particle size of the EVA emulsions. Moreover, EG50 and EG75 demonstrated an equivalent resistance toward droplet growth during the freeze–thaw stability study. This indicates that both samples provided an adequate droplet protection against neighboring collision during freezing. In a nutshell, an appropriate selection of EG concentration helps in the inhibition of droplet growth and prolongs the emulsion shelf life. It also ultimately aids to sustain the PPD emulsion performance.

**MATERIALS AND METHODS**

Diethylamine (DEA) and sodium dodecyl sulfate (SDS) were purchased from ACME Chemicals (M) Sdn. Bhd. and Hopkin & Williams Ltd. (Bendosen), respectively. Meanwhile, ethylene vinyl acetate (EVA) copolymer (25% VA), polyethylene glycol sorbitan monooleate (Tween 80), and paraffin wax were
procured from Sigma Aldrich Sdn. Bhd. Ethylene glycol and xylene on the other hand were acquired from Merck Sdn. Bhd. Distilled water was used as the base for a continuous phase mixture with DEA and antifreeze agent. Prior to the preparation of emulsions, EVA solution was first produced. EVA pellets were dissolved in xylene solvent using the slow melt dissolution technique for approximately 30 min or until the pellets were completely dissolved in the solvent. The dissolution process was carried out at 60 °C using a 300 rpm stirring speed to ensure that no air bubbles were trapped inside the solution. The melted solvent was later mixed in the continuous phase mixture containing pre-dissolved DEA surfactant solution with distilled water and antifreeze agent. The general emulsion formulation and the concentrations of the antifreeze agent are provided in Tables 4 and 5, respectively. For this mixing process, the agitation speed was increased to 500 rpm while the temperature was reduced to 50 °C.

**Table 4. Components in EVA Emulsions Used for PPD Application**

| phase           | material                  | %    |
|-----------------|---------------------------|------|
| oil phase       | EVA pellets**             | 35   |
|                 | xylene                    |      |
| continuous phase| distilled water           | 60   |
|                 | antifreeze (EG)           |      |
| surfactant      | sodium dodecyl sulfate (SDS) | 4   |
|                 | Tween 80                  |      |
| viscosifier     | diethanolamine (DEA)      | 1    |

**Table 5. Formulation of EVA Emulsions with Different EG Concentrations**

| type of antifreeze | sample code | antifreeze content (wt %) | weight percentage (%) | EVA copolymer | xylene | SDS | Tween 80 | DEA |
|--------------------|-------------|---------------------------|-----------------------|---------------|--------|-----|----------|-----|
| ethylene glycol    | EG00        | 0                         |                       | 15            | 75     | 0.5 | 3.5      | 1   |
|                    | EG25        | 25                        |                       |               |        |     |          |     |
|                    | EG50        | 50                        |                       |               |        |     |          |     |
|                    | EG75        | 75                        |                       |               |        |     |          |     |
|                    | EG100       | 100                       |                       |               |        |     |          |     |

First, emulsion samples were weighed and transferred into glass bottles to simulate a bulk storage environment during the freeze–thaw cycle. The emulsions were frozen for 22 h at a temperature beyond −10 °C before thawing it at 40 °C for additional 2 h. This cycle was repeated on a weekly basis, and characterization was carried out by progression of weeks. Any generated samples with visible oil phase after the freeze–thaw cycle were ruled out as unstable emulsions. The EVA emulsions were stored in glass bottles at room temperature (approximately 34 °C) to simulate a bulk storage environment. The samples characterization was done weekly in order to observe the effect of storage period on the droplet size. Similarly, in this experiment, any samples with visible oil phase present in the bottles were discarded as unstable emulsions. The performance assessment was conducted according to the ASTM D97 method. The emulsion samples were cooled at a specified rate, and observations were made at intervals of 1 °C for flow characteristics. The temperature at which the specimens did not display any movement was recorded as the pour point. Pour point reduction was calculated based on the differences between the pour points of treated and untreated wax solution29 using the following formula:

\[
ΔPP = PP_{before} − PP_{after}
\]

where \(ΔPP\) is the pour point reduction, \(PP_{before}\) is the pour point of untreated wax solution, and \(PP_{after}\) is the pour point of treated wax solution.

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