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An Evaluation of DEVPT effects on Water and Glycol mixture in Gas Dehydration Process

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Introduction

Today, natural gas is one of the most important fuels in our life and one of the principle sources of energy for many of our day to day needs and activities. According to [2], water content is removed from natural gas streams to meet sales specification or other downstream gas processes such as gas liquid recovery. In particular, water content level in natural gas must be maintained below a certain threshold so as to prevent hydrate formation and minimize corrosion in transmission pipelines.

The life time of a pipeline is governed by the rate at which corrosion occurs which is directly linked with the present of water content in gas which causes the formation of hydrates that reduces pipeline flow capacities, even leading to plugging and potential damage to process filters, valves and compressors. Gas dehydration can be achieved by using solid or liquid desiccants (adsorption or absorption respectively). The natural gas that comes from the well head contains water vapor that must be removed through dehydration process to avoid damage to the transportation facilities and to improve the market specification to end users.

The use of glycol for gas dehydration involves a regenerative process where the glycol is continually recovered for re-use in the succeeding cycles. Hence, glycol regeneration is the continuous recovery/removal of absorbed water from the absorbing glycol (rich glycol) or the dehydration of glycol for re-use in the succeeding cycles of dehydration, [1]

However, water constituent's glycol such as Ethylene glycol (EG), di-ethylene glycol (DEG), tri-ethylene glycol (TEG) show complete mutual solubility in liquid phase due to dehydration-oxygen bonds, and their water vapour pressure are very low, KLM Technology Group (2008).

Statement of Problem

Gas dehydration process using glycol has the major problem of loss of appreciable quantity of glycol during dehydration and regeneration processes due to the effect of water constituents.

ABSTRACT

Tri-ethylene (TEG) is used to inhibit the formation of natural gas hydrates in long transportation pipelines that convey gas from remote gas field to processing units. The degradation of glycol leads to its decomposition and reduction of its pH making it more acidic thereby, increasing its tendency to cause corrosion and subsequent blockage of production and transportation facilities. The possible effect of water on tri-ethylene glycol was ascertained in terms of changes in viscosity, pH, density and efflux time as table 1to4. Thus, the resulting effect of water on glycols (TEG) is high at room temperature and low at frozen temperature as was observed in terms of pH, viscosity and efflux time of the mixture.

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Objective

The research involves experimental investigation of effects of water on Tri-ethylene glycol (TEG) with special consideration on; density, temperature, pH, viscosity and efflux time.

Literature Review

The origin of water in natural gas can be traced to the reservoir connate water that occurs naturally with hydrocarbon. The presence of this connate water in gas gives rise to various problems during dehydration process,[6]. These problems are,

- Liquid accumulation in the wellbore
- Corrosion
- Pipeline efficiency
- Hydrate formation
- Water not needed at sales point.

According to [1], thermodynamic simulation of gas dehydration is difficult due to non-ideal liquid behavior of water and glycol mixture. According to him, the interaction is impossible to simulate with normally used thermodynamic equations of state like peng-Robinson. However, he stated that to investigate the problems with the equation of state, the water glycol mixture is simulated in MATLAB to investigate the phase behavior of the mixture. The mixture is simulated with Peng-Robinson-Stryjek-Vera equation of state. He however, concluded that the MATALAB simulations were unsuccessful in simulating the water/glycol mixture due to the non-ideal liquid behavior of the mixture.

Physical and Chemical Properties of glycol

Physically, glycols have a similar appearance as water i.e. they are colourless, odourless, clear liquid, when compared with water, glycols have higher viscosity and specific gravity at all temperature, a high boiling point, and a low freezing point. Chemically, they are water soluble and can also act as solvents for some organic compounds.



Glycol Dehydration Unit

Fig.1: Glycol dehydration unit scheme [source;ref.8] Methodology

The experiment involves a Laboratory research to determination the effect of water constituents on glycols in gas dehydration process using tri-ethylene glycol. In addition, the resulting effect of the mixture will be determined with special consideration on the density, viscosity, pH and temperature at normal condition (room temperature).

Apparatus

- Pyrometer or density bottle
- Weighing balance
- Thermometer
- pH scale
- Canon U-tube viscometer(150/601B)
- Beaker
- Pure water
- Tri-ethylene glycol (TEG)
- Ice block
- Stop watch

Procedure

Determination of density using weighing balances at room temperature

- Density bottle was weighed and recorded as 24.35g
- Density bottle with pure water was weighed and recorded as 74.12g
- Density bottle with TEG was weighed and recorded as 79.61g
- \bullet Density bottle with TEG when frozen was weighed and recorded as $80.27\mathrm{g}$
- Density of Pyrex beaker (200ml) used for mixing was weighed and recorded as 102.97g
- Density of the mixture of TEG and water when frozen was weighed and recorded.
- The mixture was taken in equal ratio as shown below and the results recorded.
- 5mL of pure water + 5mL of TEG was weighed and recorded.
- \bullet 10mL of pure water + 10mL of TEG was weighed and recorded
- \bullet 15mL of pure water and 15mL of TEG was weighed and recorded.
- \bullet 20mL of pure water+ 20mL of TEG was weighed and recorded
- \bullet 25mL of pure water+ 25mL of TEG was weighed and recorded
- The mixture was weighed to 40mL equal mixed and recorded **Determination of the temperature using thermometer**
- The room temperature of pure water was taken and recorded as $22^\circ \! \mathrm{C}$

 \bullet The room temperature of TEG was taken and recorded as 22°C

- The room temperature of the mixture of pure water and TEG at equal ratio was also taken and recorded.
- Temperature of TEG when frozen was taken as 8°C

• Temperature of mixed volume of TEG and water when frozen was taken and recorded as obtained from the viscometer chart.

Determination of pH using pH scale

- The pH of pure water was taken and recorded as 7.1
- The pH of TEG was taken and recorded as 4.033

• The pH of the mixture of pure water and TEG at equal ratio was taken and recorded.

• pH of the mixture of pure water and TEG when frozen was taken and recorded.

Determination of viscosity and measurement of the efflux time using canon u-tube viscometer (150/601b) and stop watch respectively.

• The Viscometer bathe was set at 22°C (295K)

• The thermometer was inserted on the bathe to take temperature of the bathe Fluid (Water), as a Feedback reading.

• The U-Tube that matched the Viscosity of the Fluid was selected which is Canon-U-Tube Viscometer (150/60 IB).

 \bullet The sample was suck into the U-Tube (Sample end) to the level mark (R), Clamped, and allowed to flow to level mark 1 (M1)

• It was allowed to flow to level mark 2 (M2) and the timing was immediately started.

• The timing was stopped immediately the sample reached level mark 3 (M3).

• Kinematic Viscosity; Capillary tub Constant x Efflux time in second.

• Dynamic Viscosity: Kinematic Viscosity x Density of the Sample.

• Efflux Time: This is the time it took the sample to flow from mark (M2) to mark (M3) in a Canon-U-Tube Viscometer (150/601B).

Results and Discussion

At room temperature

Weight of pyrometer or density bottle = 24.35g

Weight of density bottle with pure water = 74.12g

Density of water = 74.12g-24.35g = 49.77g

Weight of density bottle with tri-ethylene Glycol (TEG) = 79.61g

Density of TEG = 79.61g - 24.35g = 55.26g

Temperature of GLYCOL (TEG) 22° c, PH = 4.03

Efflux Time: This is the time taken for the TEG to flow through a canon U-tube viscometer, hence,

Efflux time = 5.49mins = 5x60+49 = 349secs

Kinematic viscosity: this is the viscosity taken as a product of efflux time and viscometer constant (K), thus, from chart, the viscometer constant at 22° c is, K = 0.03643251.

Therefore,

Kinematic viscosity= Efflux time x K

 $= 349 \text{secs} \ge 0.03643251 = 12.72 \text{m}^2/\text{s}$

Dynamic viscosity = Density x Kinematic Viscosity

 $= 55.26 \text{g x} \ 12.72 \text{ cm}^2/\text{s} = 702.91 \text{g/cm}1 \text{s}$

When Teg is Freezed

Temperature = $8^{\circ}c$, PH = 4.03

Weight of density bottle with TEG = 80.27g

Density of TEG = 80.27g - 24.35g = 55.92g

Efflux time = $6mins = 6x \ 60 = 360secs$

Viscometer constant at 8[°]c: This was obtained by interpolation, the reason been that the range of values of temperature for 150/607B canon U- tube viscometer as read from the chart is between 22° c to 40° c with the resulting viscometer constant (K). Hence, from 21.5° c to 0° c will be obtained by interpolation. However, after several interpolation, I was able to obtained the K value at 8^oc as, Viscometer constant (k) at $8^{\circ}c = 0.03646765$ Kinematic viscosity = Efflux time x K value $= 360 \text{secs} \ge 0.03646765 = 13.1284 \text{cm}^2/\text{s}$ Dynamic viscosity = Density x Kinematic Viscosity $= 55.92 \text{ g} \text{ x} 13. 1284 \text{ cm}^2/\text{s} = 734.14 \text{ g/cm.s}$ This Mixture Results Were Obtained, at room temperature 5ml of pure water + 5ml of TEG **Result:** Temperature $= 25^{\circ}c$ pH = 3.47Efflux time = 01.11 mins = 1x60 + 11 = 71 secs Viscometer constant (K) = 0.3642497Kinematic viscosity = Efflux time x K value $= 71 \text{ secs } \times 0.03642497 = 2.5862 \text{ cm}^2/\text{s}$ Density = 112.2g - 102.97g = 9.24gDynamic viscosity = Density x Kinematic Viscosity = 9.24g x 2.586^{2} cm²/s = 23.8962g/cm.s 10ml of pure water + 10ml of TEG **Result:** Temperature $= 25^{\circ}c$ pH = 3.36Efflux time = 01.23min = 83secs Viscometer constant (K) = 0.03642497Kinematic viscosity = Efflux time x K value $= 0.03642497 \text{ x } 83 = 3.0233 \text{ cm}^2/\text{s}$ Density = 118.26g - 102.97g = 15.29gDynamic viscosity = density x kinematic viscosity $= 15.29 \text{g x} 3.0233 \text{cm}^2/\text{s} = 46.2258 \text{g/cm.s}$ 15ml of pure water + 15ml of TEG **Result:** Temperature $= 25^{\circ}c$ pH = 3.06Efflux time = 01.18mins = 78secs Viscometer constant (K) = 0.03642497Kinematic viscosity = Efflux time x K $= 0.03642497 \text{ x}78 = 2.8 411 \text{ cm}^2/\text{s}$ Density = 132.61-102.97 = 29.64g Dynamic viscosity = density x kinematic viscosity $= 29.64 \text{g x} 2.841 \text{mm}^2/\text{s} = 84.21 \text{g/m.s}$ 20ml of pure water + 20ml of TEG **Result:** Temperature = 25° c pH = 2.87 Efflux time = 01.10 mins = 70 secs Viscometer constant (K) = 0.03642497Kinematic viscosity = Efflux time x K $= 0.03642497 \text{ x } 70 = 2.5497 \text{ cm}^2/\text{s}$ Density = 141.35-102.97 = 38.38g Dynamic viscosity = density x kinematic viscosity = 38.38g x 2.5497mm²/s = 97.8575g/cm.s 30ml of pure water + 30ml of TEG **Result:** Temperature $= 25^{\circ}c$ PH = 2.77

Efflux time = 01.13mins = 73secs

Viscosity constant (K) = 0.03642497

Kinematic viscosity = efflux time x K

 $= 0.03642497 \text{ x}73 = 2.6590 \text{ cm}^2/\text{s}$ Density =161.80g-102.97g = 58.83g Dynamic viscosity = Density x Kinematic Viscosity = 58. 83 x 2.6590 = 156.43g/cm.s 35ml of pure water + 35ml of TEG **Result:** Temperature $= 25^{\circ}c$ pH = 2.91Efflux time = 01.17 mins = 77 secs Viscosity constant (K) = 0.03642497Kinematic viscosity = Efflux time x K $= 0.03642497 \text{x}77 = 2.8047 \text{cm}^2/\text{s}$ Density =172.18-102.97g = 69.21g Dynamic viscosity = Density x Kinematic Viscosity $= 69.21 \times 2.8047 \text{ cm}^2/\text{s} = 194.11 \text{g/cm.s}$ 40ml of pure water + 40ml of TEG **Result:** Temperature = 25° c pH = 2.97 Efflux time = 01.12mins = 72secs Viscosity constant (K) = 0.03642497Kinematic viscosity= Efflux time x K $= 72 \text{ x} 0.03642497 = 2.6226 \text{ cm}^2/\text{s}$ Density =185.95g-102.97g = 82.98g Dynamic viscosity = density x kinematic viscosity = 82.98g x 2.6226cm²/s= 217.62g/cm.s Obtained when the mixture of TEG and Pure Water was frozen

Temperature = $4^{0}c$ Density = 77.94g - 24.35g pH = 4.60

Efflux time = 01:52mins = 1x60+52 = 112seconds

Kinematic viscosity = viscometer constant x efflux time

Dynamic viscosity = kinematic viscosity x density of the sample.

From chart the range of temperature for a viscometer is between 22° c to 40° c with the corresponding viscometer constant. However, when the mixture of water and TEG was frozen, the temperature dropped from 25° c (room temperature) to 4° c (frozen temperature) and the temperatures below 22° c were obtained through regression analysis with the corresponding viscometer constant as tabulated in table.1.

Results of mixed volume of glycol (TEG) and pure water when frozen

Observation

(i) It was observed that before mixture, the room temperature of pure water and TEG was the same $(22^{\circ}c)$. However when TEG was frozen, the temperature dropped to $(8^{\circ}c)$ and the efflux time at $(22^{\circ}c)$ was 349secs and 360secs at $(8^{\circ}c)$. The pH value for both pure water and TEG before mix was 7.18 and 4.03 respectively. The dynamic viscosity of TEG at $22^{\circ}c$ and $8^{\circ}c$ varied at 720.91g/cm.s and 734.14 g/cm.s respectively.

(ii) it was observed that at mixed volume of 10ml to 30ml,that the pH remained constant but decreased slowly while the dynamic viscosity keep increasing. However, the Efflux time varied at each incremental mix of the solution.

(iii) It was also observed that at 50ml mix, there was a sharp decrease in pH.

(iv) Again at 40ml to 80ml, the pH decreased slowly and sharply increased with a small value. In addition, the dynamic viscosity kept moving incrementally just as the efflux time kept changing

(v) It was also observed that as the density of the solution increased, the dynamic viscosity also increased.

(vi)It was again observed that when the mixture of TEG and water was frozen, there was a sharp drop in temperature $25^{\circ}C$ (room temperature) to $4^{\circ}C$ (frozen).

(vii)It was also observed that on freezing, the density, efflux time and the pH remained constant.

(viii)It was also observed that the dynamic viscosity was partially constant but increased slowly as the temperature dropped.

(ix) It was again observed that the pH of the mixture was more acidic at room temperature than when frozen.



Fig.2: Mixed Volume and pH (Water and Glycol)



Fig.3: Mixed volume/Dynamic viscosity (Water and Glycol)



Fig.4: Mixed Volume/Efflux time (Water and Glycol)



Fig.5: Temperature/Viscometer Constant (Water and Glycol)



Fig.6: Temperature/Dynamic Viscosity (Water and Glycol) Discussion

The fact that both pure water and tri-ethylene glycol has the same temperature before mix shows that the two are miscible $(22^{0}c)$. However, when TEG was freeze, the temperature drop to $8^{0}c$ which shows why it is necessary to dry natural gas to a certain point, as humidity in natural gas can cause pipelines to freeze and create problems for end users of the natural gas. In addition the change in efflux time at $22^{0}c$ and $8^{0}c$ shows that the viscosity of natural gas that is humid will tend to increase due to the freezing of the pipeline and process filters.

Moreover, the pH values for both pure water and TEG at room temperature are 7.18 and 4.03 respectively. This shows that the acidic content of TEG was a bit high at room temperature and the alkaline content of water was moderate. However, when equal ratios of pure water and TEG were mixed, there was a decrease in pH from 4.03 to 3.47 downward. This shows that TEG disrupts hydrogen bonding when dissolved in water. Pure TEG freezes at about 8⁰c, but when mixed with water, the mixture does not readily crystallize therefore, and the freezing point of the mixture is depressed. Because of its high affinity water, TEG is a useful desiccant. Tri-ethylene glycol (TEG) is widely used to inhibit the formation of natural gas hydrates in long multiphase pipeline that convey gas from remote gas field to a gas processing facility.

Furthermore, the dynamic viscosity kept increasing as the PH decreases slowly with variation in efflux time. This shows that the dynamic viscosity of a tri-ethylene glycol (TEG) based water solution is increased compared to that of water, as a consequence, the head loss in the piping system with TEG is increased compared to clean water. Again there was a sharp drop in pH at the 50ml mix; this indicated the maximum acidic content of the mixture. This shows that as the equal volume of the mixture increase, the concentration of the solution increases, thereby increasing the acidity of the solution.

Thus, in natural gas dehydration, the more ethylene glycol is added, the more it disrupts hydrogen bond in water vapour of natural gas which bring about dehydration of water in natural gas, hence, making tri-ethylene glycol (TEG) the ideal liquid for removal of water from natural gas stream.

In addition, the sharp drop in temperature from 25° c to 4° c when the mixture of TEG and pure water was frozen indicated the effectiveness of TEG to dehydrate water in a different temperature. This has shown the reason natural gas or crude oil forms crystals when being transported through subsea pipeline due to temperature variation, hence increasing the viscosity of the fluid and subsequent blockage of pipelines.

Table 1: Temperature, viscometer constant

Temp.(°c)	VisViscometerConst	Efflux time (secs)	HA	Density (g)	Kinematic viscosity (cm ² /s)	Dynamic viscosity (g/cm.s)
4.00	0.03647769	112	4.60	53.59	4.0855	218.944
4.50	0.03647644	112	4.60	53.59	4.0854	218.93
5.00	0.03647518	112	4.60	53.59	4.0852	218.93
5.50	0.03647393	112	4.60	53.59	4.0851	218.92
6.00	0.03647267	112	4.60	53.59	4.0849	218.91
6.50	0.03647267	112	4.60	53.59	4.0848	218.90
7.00	0.03647016	112	4.60	53.59	4.0846	218.89
7.50	0.03646891	112	4.60	53.59	4.0845	218.89
8.00	0.03646765	112	4.60	53.59	4.0844	218.88
8.50	0.03646640	112	4.60	53.59	4.0842	218.87
9.00	0.03646514	112	4.60	53.59	4.0841	218.87
9.50	0.03646389	112	4.60	53.59	4.0840	218.86
10.00	0.03646263	112	4.60	53.59	4.0838	218.85
10.50	0.03646138	112	4.60	53.59	4.0837	218.84
11.00	0.03646012	112	4.60	53.59	4.0835	218.84
11.50	0.03645887	112	4.60	53.59	4.0834	218.83
12.00	0.03645761	112	4.60	53.59	4.0833	218.82
12.50	0.03645636	112	4.60	53.59	4.0831	218.81
13.00	0.03645510	112	4.60	53.59	4.0830	218.81
13.50	0.03645259	112	4.60	53.59	4.0827	218.79
14.00	0.03645259	112	4.60	53.59	4.0827	218.79
14.50	0.03645134	112	4.60	53.59	4.0826	218.78
15.00	0.03644008	112	4.60	53.59	4.0824	218.77
15.50	0.03644883	112	4.60	53.59	4.0823	218.77
16.00	0.03644757	112	4.60	53.59	4.0821	218.76
16.50	0.03644632	112	4.60	53.59	4.0820	218.75
17.00	0.03644606	112	4.60	53.59	4.818	218.75
17.50	0.03644381	112	4.60	53.59	4.0817	218.74
18.00	0.03644255	112	4.60	53.59	4.0816	218.73
18.50	0.03644130	112	4.60	53.59	4.0814	218.72
19.00	0.03644004	112	4.60	53.59	4.0813	218.72
19.50	0.03043879	112	4.00	52.59	4.0811	218.71
20.00	0.0364375	112	4.60	53.59	4.0810	218.70
20.30	0.03043028	112	4.00	53.59	4.0809	218.09
21.00	0.03043302	112	4.00	52.59	4.0807	218.09
21.50	0.03043377	112	4.00	53.59	4.0800	218.00
22.00	0.036/3126	112	4.00	53.59	4.0004	210.00
22.50	0.03643120	112	4.00	53.59	4 0803	218.00
23.00	0.03642874	112	4.60	53.57	4 08002	218.00
23.50	0.03642074	112	4.00	53.59	4.0000	218.03
24.00	0.03642749	112	4.00	53.59	4 0707	210.04
24.50	0.03642023	112	4.00	53.59	4.0797	210.03
25.00	0.036/2372	112	4.60	53.57	4 0705	218.03
26.00	0.03642246	112	4.60	53.59	4.0793	218.61

Mixed vol. of water +TEG (ml)	Temp.(⁰ c)	Hd	Viscometer constant (K)	Kinematic viscosity (cm ² /s)	Dynamic viscosity (g/cm.s)	Efflux time (secs)	Density (g)
5 + 5 = 10	25	3.47	0.03642497	2.5862	23.8962	71	9.24
10 + 10 = 20	25	3.36	0.03642497	3.0233	46.2258	83	15.29
15 + 15 = 30	25	3.06	0.03642497	2.8411	82.9331	78	29.19
20 + 20 = 400	25	2.87	0.03642497	2.5497	97.8593	70	38.38
25 + 25 = 50	25	2.60	0.03642497	2.7683	132.7399	76	47.95
30 + 30 = 60	25	2.77	0.03642497	2.6590	156.4300	73	58.83
35+35 = 70	25	2.91	0.03642497	2.8047	194.1100	77	67.21
40 + 40 = 80	25	2.91	0.03642497	2.6226	217.6200	72	82.98

 Table 2: Result of Water and TEG at room temperature

Table 3: Mixed Volume, Efflux Time, pH & Dynamic Viscosity

Mixed vol ratio_water/TEG	РН	Dynamic Viscosity (g/cm s)	Efflux time(secs)
10	3.47	23.8962	71
20	3.36	46.2258	83
30	3.06	82.9331	78
40	2.87	97.8593	70
50	2.6	132.7399	76
60	2.77	156.43	73
70	2.91	194.11	77
80	2.91	217.62	72

Table 4: Temperature, viscometer constant and dynamic viscosity

Temp (c ^v)	Viscometer constant	Dynamic viscosity (g/cm.s)
26	0.03642246	218.61
24	0.03642749	218.64
22	0.03643251	218.67
20	0.03643753	218.70
18	0.03644255	218.73
16	0.03644757	218.75
14	0.03645259	218.79
12	0.03645761	218.82
10	0.03646263	218.85
8	0.03646765	218.88
6	0.03647267	218.91
4	0.03647769	218.94

However, the constant nature of the density and efflux time when the mixture was frozen indicated the ability of crude oil or natural gas to gel due to temperature change.

Finally, the dynamic viscosity when the mixture of TEG and water was frozen tended to be constant but increased as the temperature dropped. However, this laboratory experiment has shown that tri-ethylene Glycol (TEG) is the ideal desiccant for natural gas dehydration at any given temperature and that the ability of TEG to disrupt Hydrogen bond in water is high at room temperature than frozen temperature in terms of pH. **Conclusion**

The purpose of a glycol dehydrating unit is to remove water from natural gas liquids. When produced from a reservoir, natural gas usually contain a large amount of water and is typically completely saturated or at the water dew points. This water can cause several problems for downstream processes and equipment. At low temperatures the water can either freeze in piping or as is more commonly the case form hydrates with CO_2 and hydrocarbons (mainly methane hydrates). However, from the laboratory experiment, it was the reason why the acidity of the solution kept increasing showing how water can cause corrosion and hydrate formation in a pipeline, hence Glycol dehydration units depress the hydrate formation point of the gas through water removal [8].

The degradation of glycol leads to its decomposition and reduction of its pH making it more acidic thereby, increasing its tendency to cause corrosion and subsequent blockage of production and transportation facilities. However, the possible effect of water on tri-ethylene glycol was ascertained in terms of changes in viscosity, pH, Density and efflux time as tabulated in the tables and the graphs which showed in a long run the challenges the presence of water in natural gas can bring about as mentioned earlier on.

In conclusion, the resulting effect of water on glycols (TEG) is high at room temperature and low at frozen temperature as was observed in terms of pH, viscosity and efflux time of the mixture.

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