

CORROSION INHIBITION STUDY ON GLYCEROL AS SIMULTANEOUS GAS HYDRATE AND CORROSION INHIBITOR IN GAS PIPELINES

(Kajian Perencatan Kakisan oleh Gliserol sebagai Perencat Serentak untuk Hidrat Gas dan Kakisan dalam Saluran Paip Gas)

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Abstract

Gas hydrate inhibitors (GHI) and Corrosion Inhibitors (CI) often tend to display antagonistic behaviour in flow assurance of oil and gas. Compatible GHI and CI that have no compromises are still under research and development. Latest researches are being done on multifunctional gas hydrate and corrosion inhibitor (GHCI). Glycerol has been tested for its inhibition performance for both hydrate and corrosion in various distinguished experiments. However, glycerol's corrosion inhibition on X52 mild steel in seawater environment has never been tested. In this work, the corrosion inhibitor property of glycerol on X52 mild steel in 3.5wt.% NaCl brine solution is investigated. The concentrations of glycerol used are 400, 600, 800, 1000, 5000, and 10000 ppm. The pH and conductivity of glycerol have been measured and the relationship between pH, conductivity and corrosion has been thoroughly discussed. The performance of glycerol has been studied further based on adsorption isotherms such as Langmuir, Frumkin, Temkin and Freundlich isotherm. The Temkin isotherm shows the best fit for adsorption isotherm with R^2 of 0.97.

Keywords: hydrate, corrosion, pH, conductivity, adsorption

Abstrak

Perencat hidrat gas (GHI) dan perencat kakisan (CI) sering menunjukkan kecenderungan antagonistik dalam penjaminan aliran minyak dan gas. GHI dan CI yang tidak mempunyai kompromi ialah masih dalam penyelidikan dan pembangunan. Penyelidikan terkini dilakukan pada perencat multifungsi (GHCI) yang boleh merencat hidrat dan kakisan. Gliserol telah diuji untuk prestasi perencatannya untuk hidrat dan kakisan dalam pelbagai eksperimen yang berbeza. Bagaimanapun, perencatan kakisan gliserol pada keluli lembut X52 dalam persekitaran air laut tidak pernah diuji. Dalam penyiasatan ini, sifat perencat kakisan gliserol pada keluli lembut X52 dalam larutan garam NaCl 3.5wt.% disiasat. Kepekatan gliserol yang digunakan ialah 400, 600, 800, 1000, 5000, dan 10000 ppm. Nilai pH dan konduktiviti gliserol telah diukur dan hubungan antara pH, konduktiviti dan kakisan telah dibincangkan dengan teliti. Prestasi gliserol telah dikaji lebih lanjut berdasarkan model isoterma penjerapan seperti model Langmuir, Frumkin, Temkin dan Freundlich. Model Temkin didapati paling sesuai untuk isoterma penjerapan dengan R^2 , 0.97.

Kata kunci: hidrat, kakisan, pH, konduktiviti, penjerapan

Introduction

In the oil and gas industry, the term 'flow assurance' refers to the provision of the safe and economical delivery of hydrocarbon stream from the reservoir to the selling point through process facilities [1]. Flow assurance issues mainly involve the formation of hydrates, corrosion, asphaltenes, slugging, and emulsions [2]. Formation of gas hydrates and corrosion in pipelines are significant challenges in flow assurance [3-7]. These issues cause a considerable impact to the production in terms of the cost involved, the engineering effort and maintenance that have to be invested [8, 9]. To overcome these issues that lead to severe safety and economic losses, the industry is injecting different types of gas hydrate inhibitors (GHI) and corrosion inhibitors (CI). However, GHI and CI often tend to display antagonistic behaviour.

Along with the studies on hydrate inhibitors [10-13], and corrosion inhibitors [8, 14, 15], the researches on environmentally friendly dual functioning gas hydrate and corrosion inhibitor are ongoing as the presence of one hydrate inhibitor causes a negative impact on the corrosion inhibitor's performance and vice versa [16-19]. The understanding of the gas hydrate and corrosion phenomena is required to solve this incompatibility issue. While hydrate is an ice-like structure formed when water molecules entrap light gas molecules under high pressure and temperature, corrosion is the destructive chemical attack upon a metallic structure by its environment. Corrosion is a common electrochemical phenomenon experienced in oil and gas production [7, 20-22]. As the hydrate and corrosion inhibitors show antagonistic behaviour, it is well known that the hydrate inhibitors used in pipeline result in corrosion most of the time. Researchers have been working for decades to find a chemical that can inhibit both hydrate and corrosion in the oil and gas pipelines. Burgazli et al. [23] claimed that the corrosion inhibiting property of some gas hydrate inhibitors is an overlooked benefit to be looked upon [23, 24]. The purpose of this research is to find the dual functioning chemicals that can inhibit both hydrate and corrosion in oil and gas pipelines. In this work, glycerol showing good hydrate [25-28], and corrosion [29-31] inhibiting property in different conditions, is tested for its corrosion inhibition effect on Mild Steel X52 in 3.5wt.% sodium chloride (NaCl) solution.

Materials and Methods

Materials

Glycerol with 99.5% purity was purchased from MERCK (CAS 56-81-5) for this experiment. The 3.5wt.% NaCl brine solution, which is the corrosive medium for the corrosion study was prepared by using deionised water and reagent grade NaCl. Mild steel X52 samples with the dimensions of 10x10x5 mm have been used as the metal specimens. The composition of mild steel X52 is obtained from previous literature [32]. The metal specimen is abraded up to 800 grit, to eliminate the surface impurities. Mild steel X52 is then washed using distilled water, rinsed with Acetone to degrease, and dried. These metal samples are used for the weight loss method in the control solution of 3.5wt.% of NaCl, and the different concentrations of glycerol in the solution.

Evaluation of pH and electrical conductivity

Both pH and electrical conductivity meter are calibrated according to the user manual. SCHOTT Lab 860 probe has been used for the pH measurement. This equipment, which is used to measure the acidity or basicity of solutions has an electrode attached to the meter, and the corresponding reading can be taken from the screen. Meanwhile, for electrical conductivity, SCHOTT Lab 960 is used. This equipment has a probe with a 4-pole cell made of graphite, which enables quick and reliable conductivity measurement with an accuracy of $\pm 0.5\%$ using alternating current. The tests are done at room temperature, 298.15K. The temperature is essential for the reproducibility of the conductivity measurement. The probes are immersed directly into the beakers that contain the prepared solutions, and the results appearing on the screen are recorded once they are stabilised. The measurements are repeated to confirm reproducibility.

Weight loss method

The metal samples are accurately weighed with Mettler Toledo electronic digital weighing balance which has a sensitivity of 0.01mg and a standard deviation of ± 0.02 mg. The weighed samples are dried before being inserted into the corrosive medium. The samples are submerged into the corrosive medium, and the beakers are covered with paraffin film to ensure the solution is not exposed to foreign compounds. After the 30 days of immersion, the metal specimen was removed, washed, dried and weighed again to obtain the final mass. The corrosion rate was calculated using Equation 1.

$$CR = 8.76 * 10^4 \left(\frac{m_F - m_0}{A \rho t} \right) * 100\% \quad (1)$$

where m_F is the final mass of the metal, m_0 is the initial mass of the metal; A is the exposed surface area of metal, ρ is the density of the metal and t is the immersion period. Meanwhile, the degree of surface coverage (θ) and inhibition efficiency (η %) can be determined using equations (2) and (3).

$$\theta = \frac{Cr_1 - Cr_0}{Cr_1} \quad (2)$$

$$\eta \% = \theta * 100\% \quad (3)$$

where, Cr means corrosion rate (mm/year), θ stands for degree of surface coverage, η % means the inhibition efficiency while Cr_0 and Cr_1 mean Corrosion rate (cm/hr) without and with inhibitor.

Adsorption isotherm

Physical adsorption and chemisorption processes are the two main types of interaction in the adsorption of organic compounds onto solid surfaces. The processes are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. The experimental θ values were fitted to standard isotherms including that of Langmuir, Frumkin, Freundlich and Temkin. The value of correlation coefficient (R^2) was used to choose the best-fitting isotherm equation. The adsorption isotherm equations are shown below:

$$\text{Langmuir isotherm: } KC = \frac{\theta}{1-\theta} \quad (4)$$

$$\text{Freundlich isotherm: } \theta = KC^a \quad (5)$$

$$\text{Temkin isotherm: } KC = e^{a\theta} \quad (6)$$

$$\text{Frumkin isotherm: } KC = \frac{\theta}{1-\theta} * e^{-2a\theta} \quad (7)$$

K is the equilibrium constant of the inhibitor adsorption process, a is the parameter of interaction between inhibitor molecules adsorbed on the steel surface, and θ is the degree of surface coverage which can be calculated using equation (3).

The Langmuir adsorption model describes adsorption capacity for the coverage of surface sites by a monolayer quantitatively. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Langmuir isotherm is applied to a perfectly uniform surface, and when there is no interaction between the adsorbed molecules. The Freundlich adsorption model is used in the case of the possible formation of more than one adsorption monolayer on the surface and the sites are heterogeneous. Frumkin isotherm considers the interaction between the adsorbed species, where 1 in the equation (7) represents the number of water molecules displaced by one surfactant molecule as previously described.

Results and Discussion

Values of pH and electrical conductivity

The pH and electrical conductivity values are measured at 298.15 K. The results are tabulated in Table 1. It is observed that there is an increment in electrical conductivity and decrement in pH values with the increase of concentration. Compared to pure water, Glycerol increased electrical conductivity significantly. The increase of electrical conductivity is due to the presence of more soluble ions in the water phase that increased the mobility of ion species. The literature review shows a similar trend [33]. For pH measurements, the decrement can be attributed to the fact that glycerol in water is a weak acid with a pK_a value of 14.15 [34]. Though glycerol has three OH^- ions

in its structure, the -OH groups do not separate as an ion, making it not a base. This slightly acidic nature improves the adsorption of Glycerol onto the mild steel X52. Both the pH and conductivity values are presented graphically in Figure 1.

Table 1. pH and electrical conductivity values of aqueous Glycerol at 298.15 K

Sample Concentration (ppm)	pH	Conductivity (mS/cm)
Deionised water	6.98	0.055
400	6.82	0.7944
600	6.84	0.8753
800	6.76	0.9933
1000	6.66	0.9802
5000	6.53	1.034
10000	6.35	1.235

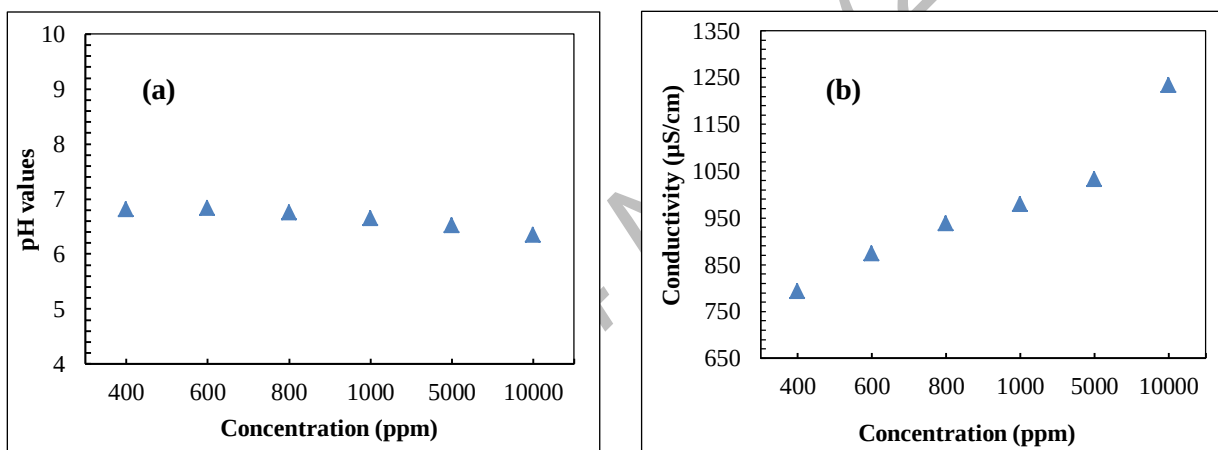


Figure 1. Results of (a) pH and (b) conductivity measurement of glycerol

Weight loss method

Based on the results from the weight-loss method, the corrosion rate and the corrosion inhibition efficiency are calculated. Table 2 tabulates the data of corrosion rate of Mild Steel X52 in the absence and presence of glycerol.

Table 2. Corrosion rate of sample and the corrosion inhibition efficiency of glycerol

Concentration (ppm)	Initial weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/year)	Inhibition Efficiency, %
Blank	3.6575	3.6416	0.0159	0.0661	0.00
400	3.6274	3.6130	0.0144	0.0604	8.68
600	3.7879	3.7730	0.0149	0.0598	9.52
800	3.7495	3.7350	0.0145	0.0588	11.04
1000	3.5634	3.5503	0.0131	0.0559	15.43
5000	3.9145	3.9064	0.0081	0.0315	52.40
10000	3.7612	3.7557	0.0055	0.0222	66.36

In the absence of glycerol, the corrosion rate of Mild steel X52 in 3.5wt.% NaCl is approximately 0.06mm/year. Addition of glycerol significantly reduces the corrosion rate and the inhibition efficiency increases with increasing concentration. From the addition of 400 ppm to 1000 ppm of glycerol to the corrosive medium, the corrosion rate reduces gradually. However, after adding 5000 ppm, there is a considerable leap in the corrosion inhibition efficiency. The increment of the inhibition efficiency might be due to the presence of optimum concentration glycerol at 5000 ppm, which is equivalent to 5wt.% the standard amount of chemical injection gas hydrate mitigation. Figure 2 clearly illustrates the effect of concentration of glycerol on the corrosion rate of the mild steel and the inhibition efficiency.

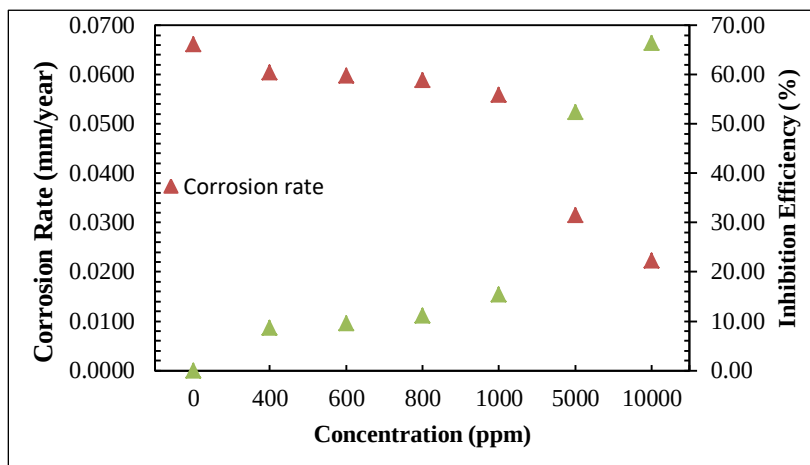
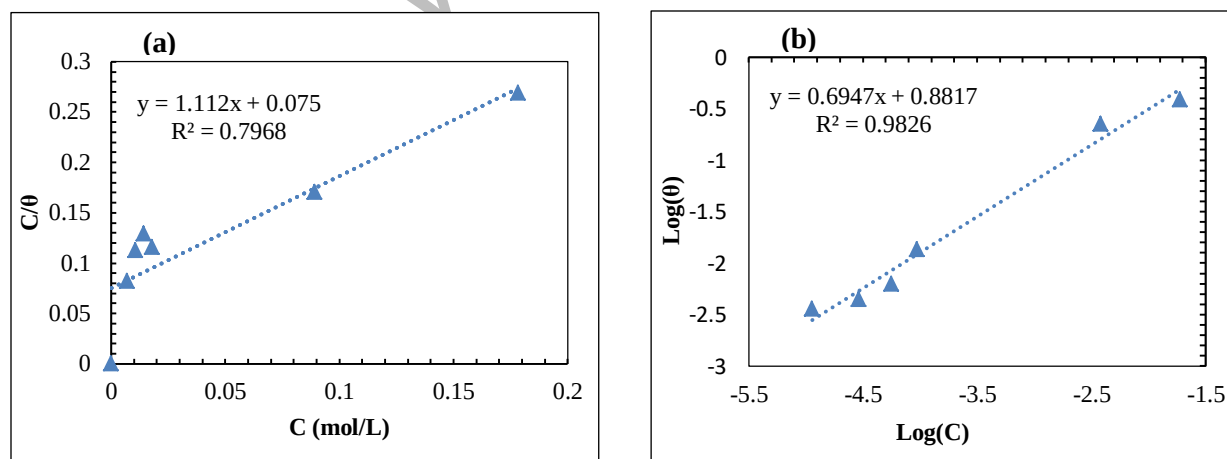


Figure 2. Effect of concentration (ppm) of corrosion rate(mm/year) and inhibition efficiency (%)

Adsorption isotherm

From the details obtained through the weight-loss method, adsorption isotherms are applied to the experimental data for further understanding of the corrosion inhibition mechanism of Glycerol. Figure 3 shows the adsorption isotherms compared with the experimental data.



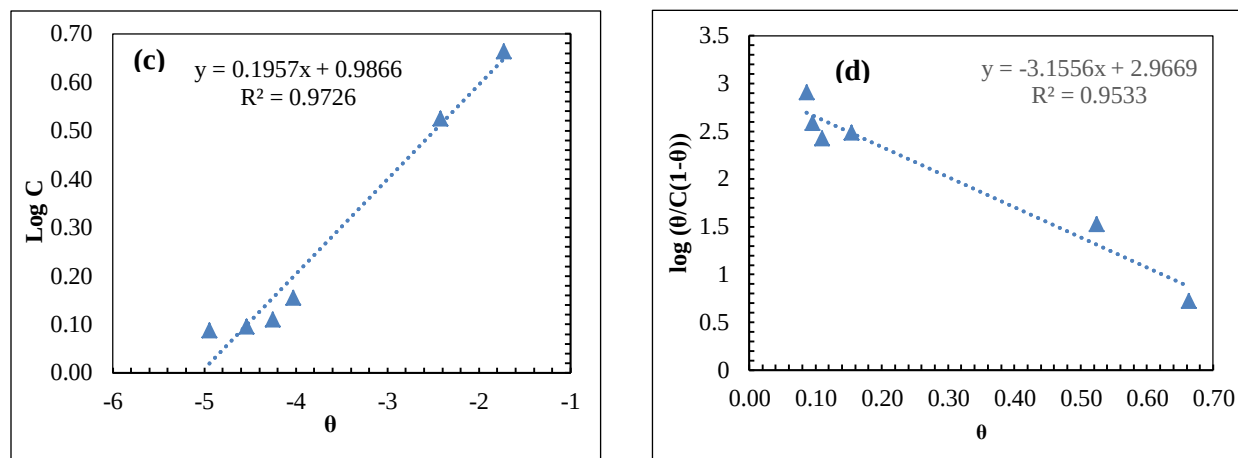


Figure 3. Adsorption isotherms fitted to experiment (a) Langmuir (b) Freundlich (c) Temkin and (d) Frumkin

All the adsorption isotherms give almost straight line to the experimental data. Based on the regression value, Freundlich Isotherm gives the best fit with R^2 equivalent to 0.97. The Freundlich isotherm equation (5) is modified to equation (8) as below to have the linear line.

$$\log \theta = \alpha \log C + \log K \quad (8)$$

From the graph plotted, it is found that the K and α values are 2.41 and 0.6947 respectively. Value of α is a measure of adsorption intensity or surface heterogeneity. If the value of α approaches zero, then it means that there is more surface heterogeneity. A value of α below unity implies chemisorption whereas α above one is an indication of cooperative adsorption[35]. The low values of K suggest that interaction between adsorbed molecules and the metal surface is not strong, indicating that the inhibitor molecules can be removed from the metal surface by any solvent molecules. Based on our results, a strong adsorption bond of chemisorptive nature could be implicated.

Conclusion

From this study, it can be concluded that glycerol has the potential to be a dual functioning gas hydrate and corrosion inhibitor. Glycerol is a common thermodynamic gas hydrate inhibitor in the oil and gas industry, and through this study, it has also been proven that glycerol has 66% corrosion inhibition efficiency at 10000 ppm (1wt%). The inhibition efficiency of glycerol shows the trend of proportionally increasing with the concentration. Although the glycerol has slightly acidic nature, the acidic nature enhances the adsorption process instead of promoting corrosion. Further researches with higher concentrations of glycerol should be done to validate the corrosion inhibition efficiency at higher concentrations of glycerol in 3.5 wt.% NaCl solution. Being an eco-friendly and cost-friendly chemical that has no adverse effect on the environment, glycerol holds vast potential towards greener application flow assurance in the oil and gas industry. It is recommended in subsequent study, influential factors of treatment temperature, CO_2 corrosion (in the absence of O_2 environment to better represent gas pipeline flowing conditions) and high-temperature high autoclave corrosion rate should be considered.

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