

Electrochemical Investigation into the Influence of Monoethylene Glycol on CO₂ Corrosion in the Presence of Acetic Acid

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ABSTRACT

This study aims to i) determine the dissociation constant (pK_a) of acetic acid (HAc) in monoethylene glycol (MEG) which is used to calculate the relative amount of undissociated HAc at different pH, and ii) investigate the influence of MEG on CO₂ corrosion of carbon steel in the presence of HAc. The study reveals that MEG increases the pK_a of HAc and obstructs its dissociation. The later effect is remarkable at pH 5 and greater. MEG also hinders the galvanic effect of ferrite and cementite by adsorbing on the active sites and reduce the corrosion rate. The inhibition efficiency of MEG is strongly dependent on its concentration. HAc is found to aggravate the corrosion of carbon steel but its activity considerably reduces with increasing MEG concentration.

Keywords: Monoethylene glycol; dissociation constant; CO₂ corrosion; acetic acid; desorption potential.

INTRODUCTION

In remote subsea production of oil and natural gas, transportation of multiphase fluids through pipelines from offshore platforms to onshore platforms or storage areas can be challenging. Water in the presence of carbon dioxide (CO₂), organic acid and hydrogen sulfide (H₂S) causes corrosion in the interior of the pipelines [1–3]. Typical concentrations of organic acids that can be encountered in the pipeline range somewhere between being 500 – 3000 ppm [4]. Acetic acid (HAc) is the dominant species among other organic acids and usually accounted for 50% to 90% of the total [5,6]. The pK_a of HAc (4.76 at 25 °C) is stronger than the carbonic acid which is generated by CO₂ [6]. Controversial effects of HAc on carbon steel corrosion in CO₂ condition was found in the literature. Some studies reported increased corrosivity in the presence of HAc [6–12], whereas others reported that HAc works as a mild corrosion inhibitor especially at room temperature by shifting the anodic potential to positive

direction [13,14]. However, when HAc is co-condensed with water on the top-of-the-line (TOL), it always aggravates the top-of-the-line corrosion (TLC) [4,15].

In addition to corrosion, the presence of water and small hydrocarbon molecules can form an ice-like substance at high pressure (above 2 MPa) and low temperature (below 20 °C) called “hydrate” which may block the pipelines and reduce in the line capacities [16]. Monoethylene glycol (MEG) has been widely used to inhibit hydrate formation due to its low toxicity and recycling capability [17–19]. MEG is also reported to possess a corrosion inhibition property [20–25]. This could be another reason that MEG is a preferred choice over other hydrate inhibitors. Typical concentrations of MEG encountered in the pipeline can vary greatly; e.g. 80 to 90 wt.% at the beginning of pipelines to 35-50 wt.% after it is diluted with condensed and/or produced water [26].

It was reported that MEG adsorbs at the steel surface and thus keeps corrosive species such as water and CO₂ derivatives away resulting in the reduction of corrosion rate [21,27,28,29]. MEG also affects physico-chemical properties of water presenting in the pipeline; e.g. density, viscosity, CO₂ solubility, and solution conductivity [27,30]. Moreover, MEG decreases the iron solubility and slow down the kinetics of FeCO₃ precipitation [26,31].

Since MEG and HAc are present in a large number of wet gas transportation pipelines, therefore, their combined effect towards pipeline corrosion is worth investigation. Because the reduction mechanism of HAc revealed that undissociated HAc is not significantly electroactive to take part in direct reduction and the main cathodic reaction is the H⁺ reduction which is called buffering effect [6,32]. In this case, the extent of corrosivity of HAc depends on its dissociation constant (pK_a), which in turn relies on the temperature, solvent property, and ionic strength of the solution [33,34]. It is expected that MEG alters the pK_a of HAc since the former affects the solution property significantly. As a consequence, the pK_a of HAc in the MEG solution is a critical factor in determining the likelihood that they will be reactants for the hydrogen evolution reaction. However, the pK_a of HAc in the aqueous and organic medium is available in the literature [35–37], whereas the same in presence of MEG is rare.

Therefore, the present investigation aims to fulfill two objectives; firstly, the dissociation constant of HAc in the presence of MEG will be studied and secondly, the influence of MEG on carbon steel corrosion in the presence of HAc will be examined.

EXPERIMENTAL PROCEDURE

Determination of pK_a of HAc in MEG solution

The dissociation constant of HAc in MEG solutions was determined by the titration method. The titrant, 0.3M of NaOH which was calibrated against the standard 0.1M potassium hydrogen phthalate, was filled in a graduated burette. The analytes were 0.03M HAc in 0%, 30%, 50% and 80% (wt.%) MEG solution. A glass vessel filled with an aliquot of analyte was placed on a hotplate and was fitted with a pH probe, a thermocouple, and a magnetic stirrer. After the analyte reached the test temperature (30 °C, 50 °C and 80 °C), the titrant was added slowly into the vessel and corresponding and steady pH was recorded. The process was repeated until the equivalence point of the titration, which was identified by the sharp change of pH, was attained. Each experiment was repeated three times and the standard deviation was below 5%. The measured pH was compensated to minimize the effect of mixed solvent [38]. The dissociation constant of HAc (K_a) in MEG solutions was then obtained based on Equation (1) [39]. K_a is a slope of a linear relationship between [H⁺] V_B vs (V_E - V_B).

$$[H^+] V_B = K_a (V_E - V_B) \quad (1)$$

where V_E and V_B are the volume of titrant added at an equivalent point and at any point, respectively, K_a is the acid dissociation constant and $[H^+]$ is the concentration of hydrogen ion with respect to any given measurements. Then pK_a was calculated from the negative logarithm of K_a .

Corrosion study of 1030 carbon steel in MEG and HAc solutions

Carbon steel (UNS G10300) specimens having the chemical composition of C 0.30%, Mn 0.75%, Si 0.25%, P 0.04%, S 0.04% with the remaining balance as iron, were used in this investigation. The mechanical properties of the steel provided by the manufacturer (Bohler, Australia) include tensile strength 520-850 MPa, yield strength 410-670 Mpa and Hardness 170-245 HB. The test specimens were machined to 6.3 mm in diameter and 10 mm in length. The specimens were soldered and cast in epoxy resin leaving approximately 0.32 cm² exposed to the test solutions. After a successive wet grinding with silicon carbide paper up to 1200 grit, the samples were rinsed with deionized water (DI) (resistance 18.2 MΩ × cm), degreased with ethanol, and then dried with nitrogen.

The solutions were 30, 50, and 90 wt.% MEG in DI water with 3 wt.% NaCl. In experiments with HAc, a total concentration of HAc was maintained at 1000 ppm. The solution was saturated with CO₂ prior to and during the experiment and temperature was maintained at 30 °C. The pH of MEG containing solution was measured following the procedure of Sandengen *et al.*[38] and maintained at 4 using either 0.1M NaHCO₃ or 0.1M HCl.

The electrochemical tests were conducted using Gamry Reference 600 potentiostat-galvanostat in a three-electrode arrangement where Ag/AgCl (3M Potassium chloride) and platinum-coated titanium mesh electrode acted as reference and counter electrodes, respectively. Open circuit potential (OCP) of specimens was monitored for 1 h to stabilize. Then, linear polarization resistance was measured for 24 h at a scan rate of 0.167 mV/s within ±10 mV with respect to OCP. Afterward, electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 10,000-0.01 Hz and AC potential amplitude of 10 mV. Finally, the potentiodynamic polarization test was performed from +250 to -250 mV with respect to OCP at a scan rate of 0.167 mV/s. All the data were analyzed using Gamry Electrochem Analyst software (Version 6.25).

RESULTS

Dissociation constant (pK_a) of HAc

pK_a of HAc in different MEG solutions at different temperatures is reported in Figure 1. It can be seen that pK_a of HAc increases with MEG concentration indicating that MEG impedes the dissociation of HAc. This is true for all 3 temperatures tested. Samini and Kenndler found a higher value of pK_a of HAc in non-aqueous solvent comparing to water and explained that 'solvent effect' and 'medium effect' played a key role in changing the pK_a [34]. The 'solvent effect' is the change in a property of the system resulting from solvent composition whereas the 'medium effect' is the property of particular solute in the different medium [34]. When MEG is added to the water, the properties of the solution change; such as viscosity, solution conductivity, pH, polarity, etc. This is referred to as the solvent effect. In the same line, the property of HAc is also changed in MEG containing solutions like dielectric constant, entropy of ionization and heat of ionization which is referred to as the medium effect.

As a consequence of an increase in pK_a , water chemistry and speciation of corrosive species in MEG containing solutions may deviate from those of water. As shown in Figure 2, in acidic conditions up to pH 4, most of the HAc remains mostly in an un-dissociated form both in water and MEG solution. Therefore, at pH 4 or below, the change in pK_a due to the presence of MEG does not affect the overall concentration of HAc. Nonetheless, as pH increases towards the neutral and alkali region, a

significantly higher concentration of the un-dissociated HAC in MEG containing solution may be expected. A higher concentration of HAC may co-condense and consequently accelerate TLC severity as HAC is volatile and the condensed water has a low buffering capacity. On the contrary, the change in un-dissociated HAC concentration may or may not affect the corrosion behavior under the bottom of the line condition as recent research has challenged the existence of the direct reduction of HAC [6,32].

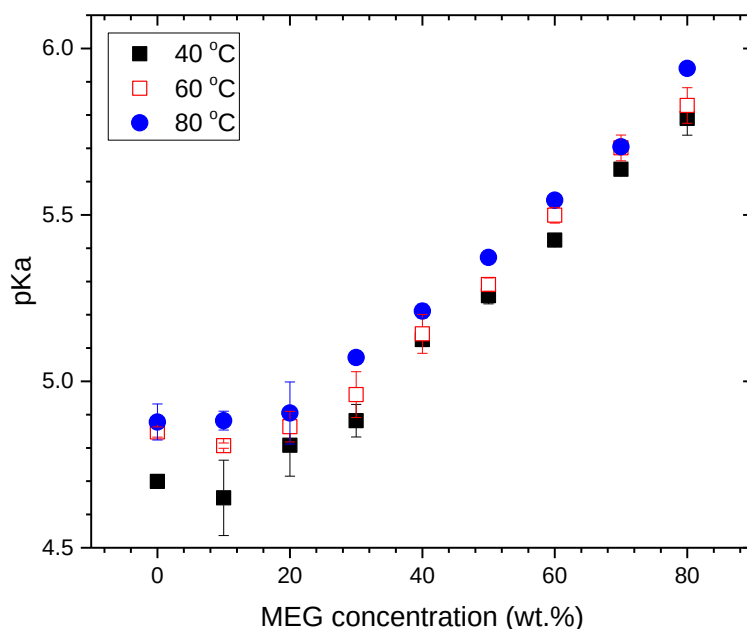


Figure 1: The variation in dissociation constant of HAC in the presence of MEG at varying temperatures

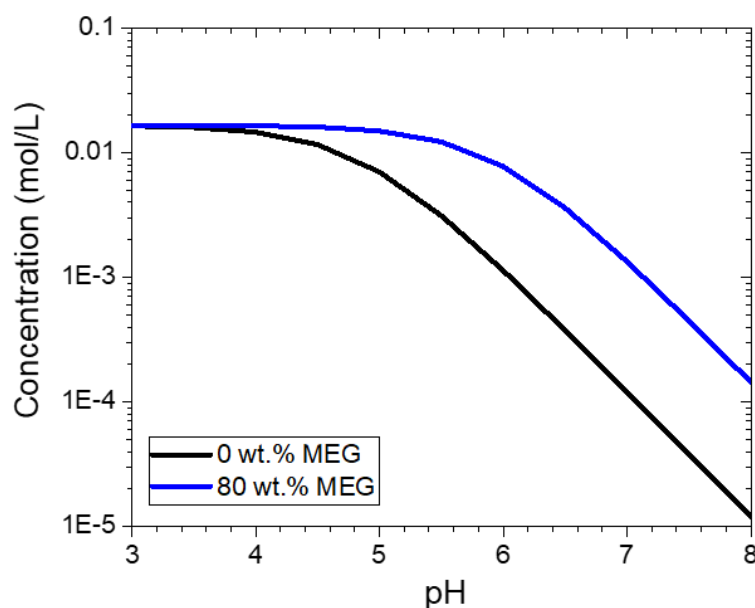


Figure 2: Concentration of undissociated HAC as a function of pH at 0% and 80% MEG

Polarization studies

Potentiodynamic polarization

Potentiodynamic polarization experiments were conducted to gain an understanding of the corrosion mechanism associated with MEG in the absence and presence of HAc by observing corrosion potential, Tafel slopes and the nature of anodic and cathodic curves. Figure 3 and Figure 4 present the polarization curves of carbon steel immersed in different MEG contents in the absence and presence of 1000 ppm HAc, respectively.

In the absence of HAc (as shown in Figure 3), both the anodic and cathodic current density decrease with increasing MEG content indicating an inhibitive performance of MEG. Corrosion potential shifts towards the anodic direction with increasing MEG contents suggesting MEG blocks the active sites. Further, the anodic branches particularly for those in the presence of MEG exhibit a desorption potential, E_d , at approximately 150 mV positive to OCP [40,41] which is absent in MEG-free solutions. Bettiss defined the desorption potential as a state of conversion of surface film from stable to unstable state [41]. The desorption potential shifts towards the noble direction with increasing MEG content (approximately -0.6 V at 30 % MEG to -0.45 V for 90 % MEG) indicating an enhanced tendency of MEG adsorption as concentration increases. This existence of E_d only in the presence of MEG can be considered as an evidence of MEG adsorption at the metal surface. Accordingly, the mass transfer limiting current also decreases with the addition of MEG. Because, solution density and viscosity affect the mass transfer coefficient of H^+ [42]. MEG being denser and more viscous solution, it impedes the proton diffusivity.

Almost similar behavior of the polarization curve is observed when experiments are conducted in the presence of 1000 ppm acetic at different MEG content as shown in Figure 4. Both the anodic and cathodic current density decrease and corrosion potential shifts toward noble direction with increasing MEG concentration.

To distinguish the interrelationship of HAc and MEG on corrosion of carbon steel, polarisation curves were rearranged as shown in Figure 5. In the absence of MEG, 1000 ppm of HAc results in an increasing cathodic current density but the anodic current density is reduced. The corrosion current density also increases in the presence of HAc. This indicates that HAc aggravates the carbon steel corrosion by accelerating the cathodic reaction. A peak, similar to E_d , is found in the anodic polarization curve in the presence of HAc and without MEG. This indicates that undissociated HAc might also adsorb on the surface. However, in the presence of 90 % MEG, the shape of the anodic curve is almost the same with or without HAc but cathodic current density slightly increases in the presence of HAc. This might indicate that the surface is saturated with MEG and therefore further adsorption by HAc does not make a difference. Therefore, the influence of HAc on carbon steel corrosion reduces drastically at 90% MEG solution.

Polarisation parameters were extracted from the curves shown in Figure 3 and Figure 4. Because the cathodic branches exhibit mass-transfer controlled behavior, only anodic polarization curves were considered for Stern-Geary constant (B) as shown in Equation (2) [43]. To make the best comparison, the portion of the anodic curve selected was within two decades, which was 30 mV apart from the corrosion potential toward a positive direction.

$$B = \frac{b_a}{2.303} \quad (2)$$

where B is the Stern-Geary constant in V and b_a is the anodic Tafel slope in V.