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Effect of major degradation products of ethylene glycol aqueous solutions on steel corrosion

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ABSTRACT

The effect of major degradation acid products of ethylene glycol (EG) aqueous solutions, namely glycolic, formic, acetic, and oxalic acids, on the corrosion behavior of low carbon steel was investigated under stirring conditions at 80 °C by means of well-established techniques for electrochemical, physico-chemical, and surface analyses. The electrochemical behavior of steel under polarization conditions is dominated by active dissolution of iron with Fe^{2+} production leading to oxide products and H^+ reduction as the cathodic counterpart. No correlation was found between the corrosion current density estimated by Tafel extrapolation method and that determined by the rate of production of Fe^{2+} under free corrosion conditions. The latter experiments revealed that the nature and the relative proportion of carboxylic acids influence the corrosion behavior of steel. The rate of production of soluble corrosion products increases with the stability and complexation ability of the organic anion towards Fe^{3+}, being more significant in the case of glycolic acid in excess with high chelation propensity. Conversely, formation of Fe^{2+} and Fe^{3+} oxalates on iron surface is promoted in the presence of oxalic acid due to a catalytic action on magnetite dissolution. The extent of above processes is compromised if hydrogen bonding interactions between different carboxylic acids are privileged.

1. Introduction

Glycols are among the most versatile compounds [1,2]. Their uniqueness is due to properties such as low volatility, viscosity, and electrical conductivity, in addition to excellent hygroscopicity, complete miscibility with water, good heat transfer capacity, and low cost. Glycols are a class of organic compounds belonging to the family of alcohols called diols of general formula $OH\text{-}R_n\text{-}OH$, where the aliphatic carbon chain connects two —OH groups. They are colourless liquids with practically no odor, and also excellent solvents for many organic compounds. Glycols are widely used as anti-freeze and cooler, chemical intermediate, gas dehydration agent, heat transfer fluid, solvent, etc. The most important member of glycols family is the mono ethylene glycol $HO\text{-}CH_2\text{-}CH_2\text{-}OH$ (EG) [2].

EG has been proposed as the best choice for heat transfer applications because of the lower viscosity and superior heat transfer efficiency with respect to other glycols such as propylene glycol, which is considered when toxicity is a concern [2,3]. A minimum concentration of 25–30 wt% in water has been recommended for obtaining thermal performances comparable to that of water, bactericide and fungicide actions, and corrosion protection. The quality of water is an important issue, in particular the contents of Cl^- (corrosive), Ca^{2+} and Mg^{2+} (scale-forming) should be below 25 and 50 ppm, respectively, if tap water is used. The heat transfer performance of water-based EG fluids decreases with time because of absorption of moisture from the environment and, more importantly, due to EG thermal oxidation in the presence of oxygen leading to carboxylic acids as main degradation products [4,5]. The most common acids found in degraded real fluids are acetic (AA), formic (FA), glycolic (GA), and oxalic (OA). Table 1 reports the corresponding schematic structures, dissociation reactions and standard equilibrium dissociation constants (pKa) [6]. The former three acids are monoprotic carboxylic acids, being GA an hydroxy acid (α-hydroxyacetic acid) and AA the most basic according to the pKa values (Table 1). The acid strength of dicarboxylic OA, if completely dissociated, decreases and becomes comparable to that of FA and GA. Another important issue is the metallic material of the heat transfer system that may catalyze the hydrothermal oxidation of EG and in turn corrode faster as a result

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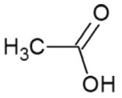
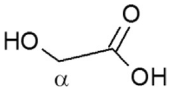
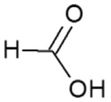
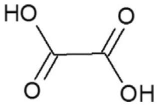
Table 1
Carboxylic acids structures, dissociation reactions, and standard equilibrium pKa values.

Carboxylic acid	Schematic structures	Dissociation reaction	pKa [5]
Acetic acid (AA)		$CH_3COOH \leftrightarrow CH_3COO^- + H^+$	4.76
Glycolic acid (GA)		$OHCH_2COOH \leftrightarrow OHCH_2COO^- + H^+$	3.83
Formic acid (FA)		$HCOOH \leftrightarrow HCOO^- + H^+$	3.75
Oxalic acid (OA)		$H_2C_2O_4 \leftrightarrow HC_2O_4^- + H^+$ $HC_2O_4^- \leftrightarrow C_2O_4^{2-} + H^+$	1.25 3.81

of pH decrease, among other factors [[4,5,7–10], and ref. therein]. Major limitations of mild steel and cast iron are the low heat capacity and the high susceptibility to corrosion, in comparison to Cu and Al alloys. Nonetheless, iron-based materials are still the most used due to practical considerations. Buffering and inhibition are common practices for corrosion prevention [11]. Besides specific operative conditions (EG concentration, temperature, pressure, O_2, additives), the nature of the metal in contact with EG aqueous solution contributes to the variety of possible reactions that lead to different organic sub-products.

The mechanistic pathways of EG hydrothermal oxidative decomposition involve aldehydes such as glycoaldehyde, acetaldehyde and formaldehyde, in addition to FA, as intermediate compounds. Aldehydes being involved in low and high barrier paths of EG degradation have been theoretically predicted also [12]. These sub-products may undergo self- and cross-disproportionation reactions in hot water in absence of catalysts to form FA and methanol [13]. In addition, acid-catalyzed C—C bond formation from formaldehyde and FA may leads to GA, being the reaction more selective with FA in excess. From studies of thermal degradation of EG in the presence of iron based materials [4 and ref. therein], the following general sequence has been proposed: formation of OA and AA, then conversion of OA into FA with prolonged heating, and finally dissociation of AA and FA to form carbon dioxide, which converts into carbonic acid upon reaction with water. Salts sub-products of ferrous acetate, formate and carbonate were considered also. Ion chromatography analysis of uninhibited EG solutions (75 wt%) after 90 days of operation at 95 °C in crude oil preheating tubes indicated AA and FA as major sub-products [4]. Different results have been obtained from systematic studies using real fluids of solar collector systems [5] and laboratory-made solutions [7–10]. Ion chromatography and mass spectrometry analyses of degraded aqueous solutions of EG (50–70 wt%) after operation within common temperature range of service (75–130 °C) and in the presence of dissolved O_2 indicated GA as main constituent while OA and FA were detected in smaller amounts. The hydrothermal degradation of EG was importantly accelerated after placing metallic Cu in the reaction medium, differently from Al for which higher amounts of FA rather than of GA were detected. In addition, production of CO_2 on the expense of O_2 consumption by reactions with free radical intermediates of EG decomposition was more important as temperature increased and in the presence of Cu [10]. Investigations on electrochemical corrosion of Al alloys have shown that O_2 reduction controls metal dissolution in EG solutions at ambient temperature [14,15]. Higher susceptibility to corrosion has been reported in hot alkaline EG solutions to which GA was intentionally added, being associated to Al^{3+} complexation by glycolate [16]. A very recent investigation of EG electrooxidation on iron-group nanoalloy catalysts have demonstrated, both experimentally and theoretically, that GA is generated at the first stage of the EG oxidation to form OA [17]. Participation of organic intermediates during corrosion of steel is not limited to EG solutions but extends to aqueous CO_2 solutions [18] and alcohols [19].

The electrochemical corrosion of steel in acid solutions is subject of intense research, in part due to its significance in oilfield applications [11]. Studies in aqueous solutions of EG have considered the effect of galvanic corrosion [20], acidity (HCl) [21], EG concentration [20,22], solution rotation speed [23,24] and presence of inhibitors [22–24]. Concerning the carboxylic acids degradation products, OA [25–27], AA [28–31] and FA [29,31–33] have attracted major interest, differently from GA [34]. In addition, mineral acids and/or supporting electrolytes, as well as Cl^-, have been intentionally added to the test solutions. Electrochemical methods such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), in combination with weight loss measurements, have been mostly used. The polarization behavior usually manifests active corrosion. The possible relation between electrochemical decomposition of EG and electrochemical corrosion of steel, in particular under hydrodynamic conditions at high temperatures, has ever been suggested.

In this paper, the corrosion of steel is investigated at 80 °C in stirred solutions of EG at 30 wt% in tap water containing mixtures of AA, GA, FA and OA (Table 1) in trace amounts to simulate degraded EG solutions of real fluids. In addition to EIS and potentiodynamic polarization techniques, experiments under free corrosion conditions were carried out. These consisted in the measurement as a function of time of the free corrosion potential, solution pH and conductivity, and concentrations of Fe^{2+} and Fe^{3+}. Possible alteration of the acid-based equilibrium with corrosion