

DEGRADED AQUEOUS GLYCOL SOLUTIONS: pH VALUES AND THE EFFECTS OF COMMON IONS ON SUPPRESSING pH DECREASES

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Received 17 May 1984; in revised form 30 August 1984

Aqueous solutions of ethylene glycol and propylene glycol are used as heat transfer liquids in flat-plate solar collector systems. Both of the glycols are susceptible to thermal oxidative reactions, which produce organic acids with a resulting decrease in pH of the solutions. The effects of temperature, metals, common ions and oxidation conditions (aeration/deaeration) on the thermal stability of the glycol solutions were evaluated based on measuring changes in pH. Aerated heated glycol solutions produced acidic solutions within 3360 h (140 d) of testing, when in contact with either metallic aluminum or copper. Common ions (anions of the acid degradation products) were effective in suppressing decreases in pH, especially when aluminum was present.

1. Introduction

Aqueous solutions of ethylene glycol and propylene glycol are commonly used heat transfer liquids in flat-plate solar collector systems. Both glycols are susceptible to thermal oxidative reactions, which produce organic acids with a resulting decrease in pH of the aqueous mixtures. Decreases in the pH of the heat transfer liquids could accelerate the corrosion of metallic components of collector systems [1-4]. Usually buffers are added to glycol-based solutions to maintain the pH at a desired level. Buffers, however, are gradually consumed, and if the liquids are not rebuffed or replaced, corrosive conditions can develop. A review of the use of buffers in glycol solutions has recently been presented [5]. Information on glycol degradation has been developed largely by the automobile coolant industry. Experience with automobile antifreezes, however, is probably not adequate to assess their stabilities under various collector operating conditions [1]. Studies, therefore, have been carried out to investigate the degradation products and their effects on the pH [4]. In the current investigation, the effects of temperature, oxidative conditions (aeration/deaeration), and test metals on pH changes are reported. In addition, the study investigated the possibility of suppressing decreases in the pH by using anions of the acid degradation products (common ion effect) as buffers. The effect of the addition of common ions to the glycol solutions on factors other than pH which influence corrosion was not investigated.

2. Common ion effect

The major acidic degradation products of ethylene glycol have been identified as oxalic, glycolic and formic acids, while for propylene glycol they are oxalic, lactic, formic and acetic acids [4]. These are weak acids which are only partially dissociated in aqueous solutions. For monobasic acids, their dissociation may be expressed by

$$K_a = [H^+][R^-]/[HR], \quad (1)$$

where $[HR]$ is the concentration of the organic acid, $[H^+]$ is the concentration of hydrogen ions, $[R^-]$ is the concentration of the organic anions and K_a is the acid dissociation constant.

Rearranging the equation to

$$[H^+] = K_a[HR]/[R^-] \quad (2)$$

indicates that the concentration of the hydrogen ion, H^+ , varies inversely with the concentration of the organic anion, R^- . By the addition of common anions, therefore, the dissociation of the organic acid can be suppressed. That is, if a soluble salt containing the common ion, R^- , is added to an aqueous glycol solution, the formation of H^+ and a decrease in pH should be suppressed. The effects of common ions on changes in pH of the glycol solutions were investigated by using those salts listed in table 1. The common ions added to either the ethylene glycol or propylene glycol solutions were those corresponding to the anions of the major acidic degradation products of the respective glycol [4]. In the presence of copper, ethylene glycol solutions yielded primarily glycolic acid and propylene glycol solutions gave primarily lactic acid. The relative concentrations of the common ions added to the glycol solutions were based on the concentrations of the degradation products found by the ion chromatographic analysis of glycol solutions which had been heated for 12 weeks at 100°C with aeration [4].

Table 1
Common ions added to glycol solutions

Glycol ^{a)}	Common ions	Concentrations of common ions ^{b)} (g/l)
Ethylene glycol	sodium glycolate	50
	sodium formate	5
	sodium oxalate	0.5
Propylene glycol	calcium lactate	25
	sodium formate	5
	sodium acetate	5
	sodium oxalate	0.5

^{a)} 9 mol/l aqueous solutions.

^{b)} Concentrations based on volume of aqueous glycol solution.

3. Experimental

3.1. Apparatus and materials

Degradation studies of the aqueous glycol solutions were carried out using the apparatus shown in fig. 1. Glycol solutions, 225 ml, were placed in cylindrical glass reaction tubes of 260 ml capacity. Water cooled condenser tubes were connected to the reaction tubes to minimize the loss of the glycol solutions. The reaction solutions were maintained at the temperatures to within $\pm 1^\circ\text{C}$ by immersion in an oil bath. The temperatures used were 75, 86 and 101°C . Test solutions were either deaerated with high purity $\text{N}_2(\text{g})$ or aerated with laboratory air which passes through gas dispersion tubes immersed in the solutions. Experimental details are presented in table 2.

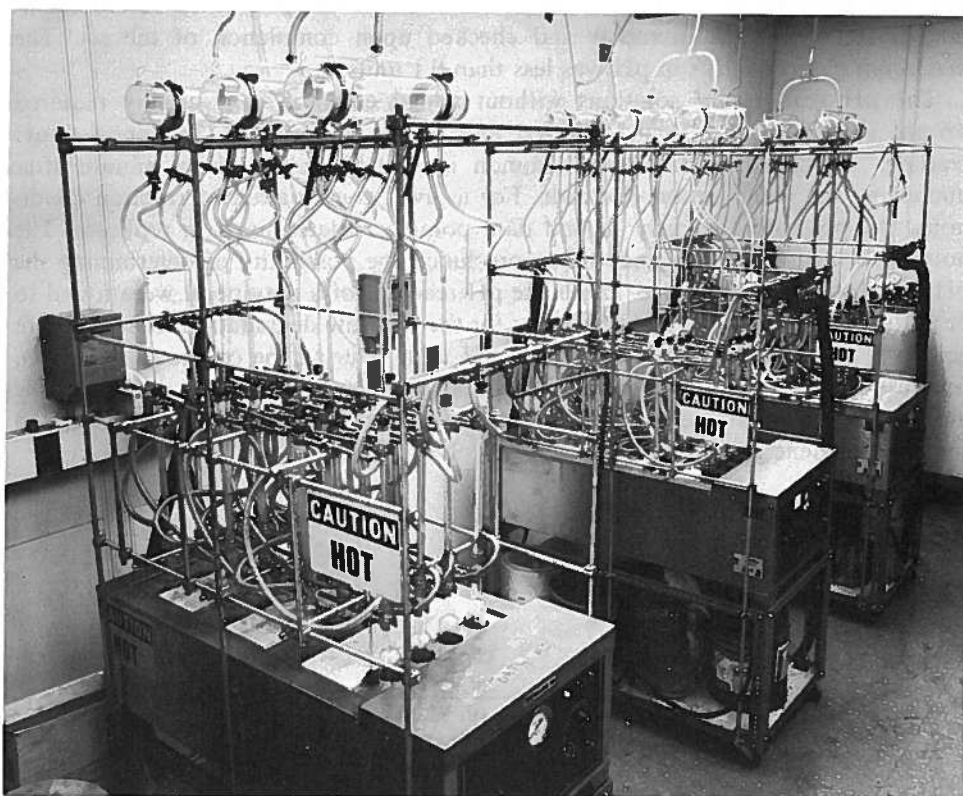


Fig. 1. Apparatus for thermal oxidative degradation studies. Three oil baths were used, each holding 24 glass reaction vessels.

Common ion solutions (table 1) were prepared and by dissolving reagent grade chemicals in distilled water. Reagent grade ethylene glycol and 1,2-propylene glycol were vacuum distilled and diluted to 50 and 66 vol% with the common ion solution, respectively, to give 9 mol/l aqueous solutions.

The effect of metallic aluminum and copper on glycol degradation also were investigated. Coupons of 1100 aluminum and 110 copper alloys ($19.2 \times 50.0 \times 0.80$ mm³) were placed in the test solutions immediately prior to heating them. For each combination of reaction conditions at each temperature, replicate degradation reactions were conducted.

3.2. Measurement of pH

For each measurement a 4–6 ml aliquot was taken from the reaction tubes, transferred to a stoppered vial, and allowed to cool to ambient temperature ($23 \pm 2^\circ\text{C}$). Measurements of the pH were made on stirred samples under N₂(g), using a combination pH electrode and a high impedance voltmeter as required in ASTM D 1287 [6]. The meter was calibrated between 3.0 to 12.0 pH units using pH buffer solutions specified in ASTM D 1287 [6]. Calibration was performed before beginning a set of 16 measurements and checked upon completion of the set. The maximum observed drift in pH was less than 0.1 units.

The pH readings of solutions without added common ions usually required several minutes before they stabilized and could be recorded. In contrast, pH readings of solutions containing common ions stabilized within a minute after immersing the combination electrode. For a given combination of reaction conditions, the pH value of every second data point was determined in replicate. The number of analyses to be undertaken precluded the possibility of determining the pH value of each point twice. Duplicate pH readings of a data point were found to be within ± 0.1 pH units. The pH values for the replicate degradation reactions were generally determined to be within ± 0.5 pH units. During the course of the study, five test solutions of both ethylene glycol and propylene glycol were prepared. The mean pH values of the test solutions were 8.1 (standard deviation of 0.30 pH units) for both ethylene glycol and propylene glycol.

Table 2
Experimental details

Temperature	75, 86 and 101°C
Solution compositions	9 mol/l aqueous solution of ethylene or 1,2-propyleneglycol
Common ions	added (see table 1); not added
Metals used	1100 Al alloy; 110 Cu; none
Aeration condition	laboratory compressed air or purified N ₂ (g)

4. Results and discussion

4.1. Solutions without common ions

The pH values of aerated solutions without common ions decreased significantly after relatively short periods of heating. For example, when heated a 75°C, the pH value of both ethylene and propylene glycol solutions in contact with copper decreased to below 6 within 500 h (fig. 2). Subsequently, smaller decreases in pH were observed and at 3360 h (140 d) the pH values were 4.8 for the ethylene glycol solution and 4.6 for the propylene glycol solution (table 3). In contrast to solutions in contact with copper, the pH of the solutions having no metal present decreased at a slower rate. The pH values of solutions having aluminum present were slightly higher than those obtained in the absence of any test metal (fig. 2). Even with aluminum, however, the pH values of both glycol solutions were less than 7 units after 1500 h of heating at 75°C, and decreased to 6.3 units for the ethylene solution and 5.9 units for the propylene solutions after 3360 h (table 3).

At higher temperatures, 87 (fig. 3) and 101°C (fig. 4), the pH curve when copper was present had a similar shape to that obtained at 75°C, but was depressed to somewhat lower pH values. For example, the pH values for ethylene glycol after 3360 h of heating were 4.8 at 75°C, 4.5 at 86°C and 3.4 at 101°C (table 3). The pH

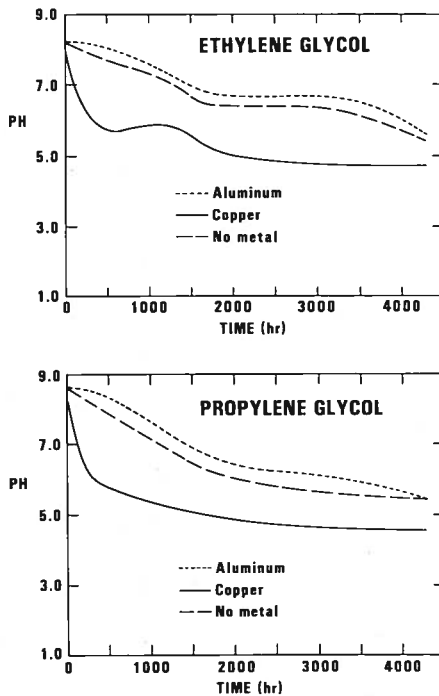


Fig. 2. Change in pH values of aerated glycol solutions at 75°C.

Table 3
pH of aerated aqueous glycol solutions at 3360 h (140 d)

Glycol ^{a)}	Common ions ^{b)}	Temp. (°C)	pH		
			none	copper	aluminum
Ethylene	none	75	6.1	4.8	6.3
	none	86	4.3	4.5	4.7
	added		7.1	6.7	10.1
	none	101	2.4	3.4	3.9
	added		7.8	5.3	9.8
1,2-propylene	none	75	5.8	4.6	5.9
	none	86	5.4	4.1	5.3
	added		7.2	4.9	8.3
	none	101	2.0	3.7	3.7
	added		7.1	5.1	7.5

a) 9 mol/l aqueous solutions.

b) Composition given in table 1.

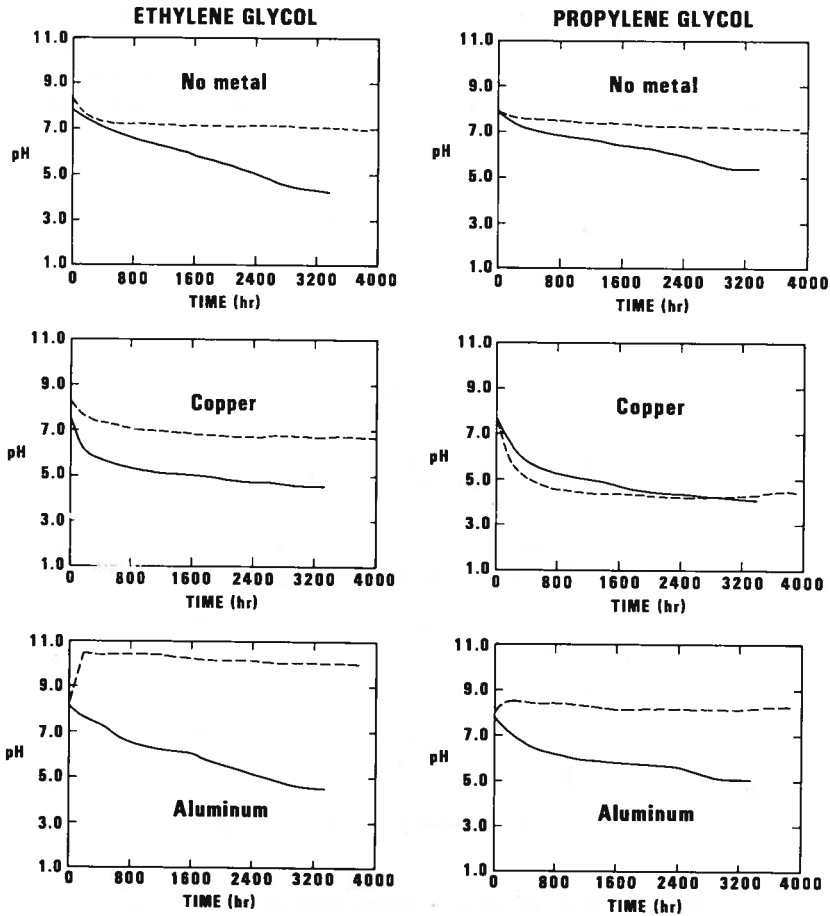


Fig. 3. Change in pH values of aerated glycol solutions at 86°C. Broken lines indicate that the solutions contained common ions, solid lines indicate that common ions were not added.

curves obtained in the presence of aluminum and in the absence of any test metal were clearly more temperature sensitive than when copper was present. The lowest pH values were measured for glycol solutions heated at 101°C in the absence of any test metal. Under these conditions, the pH values after 3360 h were 2.4 units for the ethylene glycol solution and 2.0 units for the propylene glycol solution.

4.2. Common ions

Common ions (listed in table 1) were added to glycol solutions prior to being heated at 86 and 101°C. Their effects on changes in pH values of aerated glycol solutions are indicated by the broken line curves in figs. 3 and 4. The effectiveness of the common ions in suppressing reductions in pH were dependent on the presence of metal and decreased in the sequence: aluminum, no metal, copper. The combination

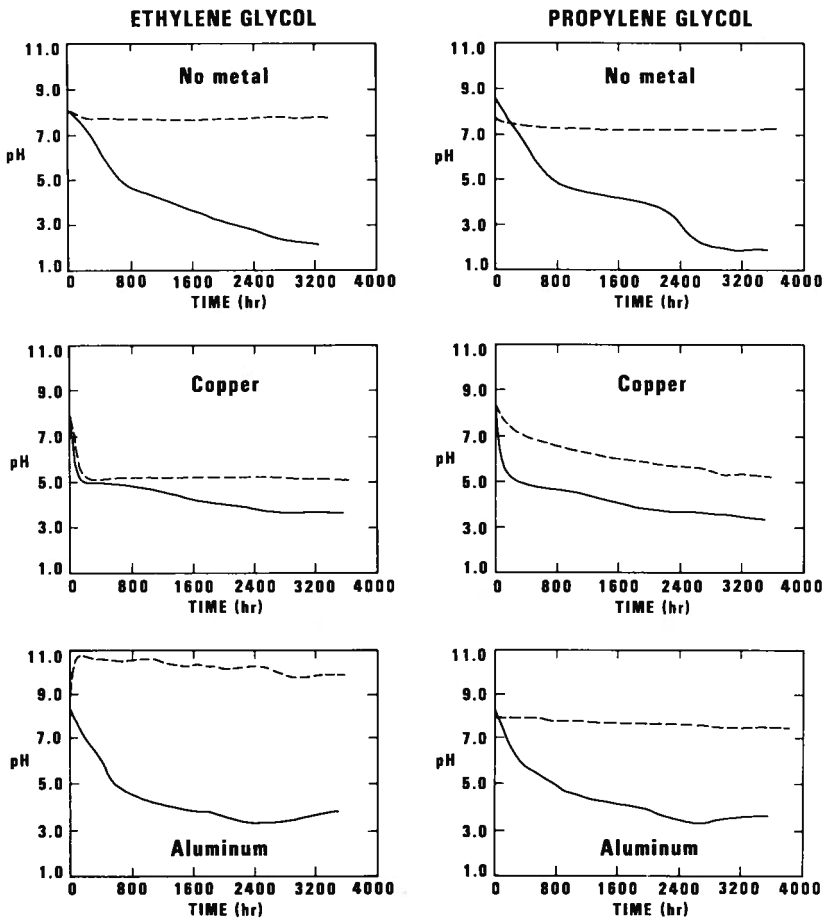


Fig. 4. Change in pH values of aerated glycol solutions at 101°C. Broken lines indicate that the solutions contained common ions, solid lines indicate that common ions were not added.

of common ions and aluminum, with one exception, produced an increase in pH. This pH increase may be attributable to the amphoteric behavior of aluminum [7]. The exception occurred when aerated propylene glycol was heated at 101°C. Under these conditions a decrease of 0.6 pH units was measured after 3360 h of heating (table 3).

Common ions were somewhat less effective when aluminum was not present; e.g. the pH of aerated ethylene glycol heated at 86°C for 3360 h was reduced to 7.1 but was 10.1 in the presence of aluminum. Under the same conditions without common ions, however, the pH was reduced to 4.3 units. The effects of common ions when no metal was present were most noticeable at 101°C. After 3360 h of heating at 101°C the pH of aerated ethylene glycol was 2.4 units and that of propylene glycol was 2.0 units compared to respective values of 7.8 and 7.1 units when common ions were added.

Common ions were less effective when copper was present. Only with the exception of ethylene glycol heated at 86°C were the pH values of the solution above 6 units after 1600 h. After 3360 h all the pH values of glycol solutions in contact with copper were acidic, ranging from 6.7 to 5.2 units for ethylene glycol and 5.1 to 4.9 units for propylene glycol.

4.3. Aeration conditions

A limited study was performed to determine the effects of aeration conditions on degradation of glycol solutions and the results are given in table 4. Under identical test conditions, the glycol solutions which were deaerated with N₂(g) produced less acidic solutions than the aerated solutions. The observed decrease in pH values of the deaerated solutions after 3360 h of testing is considered to have been caused largely by some exposure of the solutions to air while extracting samples for the pH measurements.

Table 4
Comparison of effects of N₂(g) and air on pH of aqueous glycol solutions ^{a)}

Glycol ^{b)}	Common ions ^{c)}	Conditions	pH		
			T = 75°C	86°C	100°C
Ethylene	none	N ₂ (g)	7.4	6.1	6.0
		air	6.1	4.3	2.4
	added	N ₂ (g)		7.7	7.5
		air		7.1	7.8
1,2-propylene	none	N ₂ (g)	7.0	4.8	4.8
		air	5.8	5.4	2.0
	added	N ₂ (g)		7.2	7.3
		air		7.2	7.1

^{a)} Based on 3360 h (140 d) of testing. No test metal present.

^{b)} 9 mol/l aqueous solutions.

^{c)} Composition given in table 1.

4.4. Glycol

As indicated by changes in the pH, little difference was observed in the chemical stability of aqueous ethylene glycol and propylene glycol solutions except when both aluminum and common ions were present. Under these conditions, the pH values of aerated ethylene glycol solutions at 86 and 101°C were about 2 pH units higher than those for propylene glycol after 3360 h of testing.

5. Summary and conclusions

This study investigated the effects of several variables on the thermal stability of aqueous ethylene glycol and propylene glycol solutions. Solutions without common ions were heated at 75, 86 and 101°C with aeration and in the presence of metallic copper aluminum, or without a metal present. The extent of glycol degradation was monitored by periodically measuring the pH value of the test solution. All solutions produced acidic degradation products as indicated by a decrease in their pH values. As expected, the decrease in pH of the reaction solutions was temperature dependent with the lowest pH values resulting from heating at 101°C. When heated with aeration for 3360 h (140 d) at 101°C in the presence of metallic copper or aluminum, the glycol solutions showed a decrease in pH value to less than 4. Under these conditions in the absence of metal, the pH of the ethylene glycol solution dropped to 2.4 and the pH of the propylene glycol solution dropped to 2.0. It was also found that for a given set of reaction conditions (i.e. temperature, presence or absence of metal), the two glycols showed comparable decreases in the pH values of their aqueous solutions.

The study also examined the effectiveness of using common ions to prevent a decrease in the pH values of the glycol solutions upon heating. The common ions used were the anions of the organic acids previously found to be produced by the thermal oxidative degradation of aqueous ethylene and propylene glycol solutions. The effect of the common ions was found to be somewhat glycol dependent. Decreases in pH values of the ethylene glycols in contact with aluminum were effectively suppressed when common ions were added. Common ions were less effective in suppressing pH changes of propylene glycol solutions. When copper was present, acidic solutions were produced even when common ions were added to the glycol solutions. The common ion effect for solutions having no metals was intermediate between the common ion effects found when either metallic aluminum or copper was present.

Acknowledgements

This study was sponsored by the US Department of Energy, Office of Solar Heat Technologies. The authors wish to acknowledge with thanks the assistance of Mr. Nat Waters, National Bureau of Standards, in the experimental aspects of this study.

Special appreciation and thanks are given to Dr. James J. Filliben, statistician, National Bureau of Standards, for his assistance in data reduction and analysis.

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