

AN INVESTIGATION OF THE DEGRADATION OF AQUEOUS ETHYLENE GLYCOL AND PROPYLENE GLYCOL SOLUTIONS USING ION CHROMATOGRAPHY

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Aqueous solutions of ethylene glycol and propylene glycol produce acidic degradation products upon thermal oxidation. This results in a decrease in pH of the aqueous solutions which could accelerate the corrosion of metallic components of solar collectors. The increase in the concentrations of degradation products in solution was measured over time using the Ion Chromatography Exclusion (ICE) method of analysis. Variables affecting the thermal oxidation considered in the investigation were temperature, the presence of metals and oxidative conditions (aeration/deaeration). Acidic degradation products were produced under all conditions. The presence of metallic copper in aerated glycol solutions resulted in the greatest extent of degradation. Comparisons were made between the pH values of the thermal oxidatively degraded glycol solutions and the concentrations of degradation products. It was found that different solutions having comparable pH values contained significantly different amounts of degradation products. It was concluded that the extent of degradation of the glycol cannot be used as an indicator of the magnitude of the decrease in pH which the glycol solution may undergo during thermal oxidation in the presence of metals.

1. Introduction

Flat-plate solar collector systems using aqueous heat transfer fluids must be provided with freeze protection, unless located in warm climates. A common method of freeze protection is to use antifreezes as heat transfer fluids. Aqueous solutions of ethylene glycol and propylene glycols are commonly used, accounting for more than one-third of the fluids used in flat-plate solar collectors [1]. Although these glycol solutions have satisfactory heat transfer properties, thermal oxidation of the glycols under operating conditions produces organic acids. The result is a lowering of the pH values of heat transfer fluids which could accelerate corrosion of metallic components of collector systems [1-4]. To guard against the development of acidic corrosion conditions, the glycol solutions are buffered to maintain the desired pH level. Periodic measurement of the pH and reverse alkalinity of the glycol solutions has been recommended to assure that the fluid remains properly buffered and that corrosive conditions do not develop [3].

Although several studies [3–6] have been conducted on the effect of glycol degradation on the rates of corrosion of metallic collector components, little attention has been given to the rates of glycol degradation under collector operating conditions. This lack of information on glycol degradation makes it difficult to predict the time to fluid breakdown or to draw conclusions about the lifetimes of aqueous glycol-based heat transfer fluids [3]. Recent studies have been conducted using ion chromatography to identify the major acidic degradation products of aqueous ethylene and propylene glycols [7]. Additional studies have been carried out to investigate the effects of temperature, oxidative conditions and the presence of metals on changes in pH values of aqueous glycol solutions and to evaluate the effectiveness of common ions (anions of the acidic degradation products) in suppressing decreases in pH [8]. In the present investigation, increases in the amount of glycol degradation products with time are reported as a function of temperature, oxidative conditions (aeration/deaeration) and the presence of metals. Comparisons are made between the pH values of the degraded glycol solutions and the amount of degradation which the glycols have undergone.

2. Ion chromatographic analysis of degraded glycol solutions

Ion chromatography is a liquid chromatographic technique for the analysis of ionic species in aqueous solutions [9]. The use of ion chromatography for the analysis of degraded aqueous ethylene glycol and propylene glycol solutions has previously been described [7]. The major acidic degradation products from the thermal oxidation of ethylene glycol have been identified as oxalic, glycolic and formic acids. For propylene glycol, they are oxalic, lactic, formic and acetic acids. Ion chromatography thus provides a means for determining quantitatively the concentrations of the acidic degradation products in the parts per million (ppm) level. However, a technique for the total analysis of the degradation products in buffered glycol solutions has not been developed.

3. Experimental

3.1. Ion chromatographic apparatus and analytical procedure

The Ion Chromatography Exclusion (ICE) method, as previously described [7], was used for the analysis of the degraded glycol solutions. For details concerning the procedures, apparatus including chromatography columns and instrument calibration, the reader is referred to this reference.

3.2. Glycols

The ethylene glycol and 1,2-propylene glycol reagents were distilled under vacuum before use. Only the middle distilling fractions were used in the degradation studies.

Ion chromatographic analysis of the distilled glycols did not detect the presence of any acidic degradation products.

3.3. Degradation conditions

The distilled ethylene glycol and propylene glycol reagents were diluted to 50 and 66 vol%, respectively, with distilled water to give 9 mol/l aqueous solutions. The degradation studies of the aqueous glycol solutions were carried out in constant temperature oil baths. Two hundred and twenty five (225) ml of the aqueous glycol solutions were placed in cylindrical glass reaction tubes of 260 ml capacity. The reaction tubes were lowered into the oil baths whose temperatures were maintained constant to within $\pm 1^\circ\text{C}$. Three oil baths with temperatures of 75, 86 and 101°C were used. Water-cooled condenser tubes were connected to the reaction tubes to minimize loss of the glycol solutions during heating.

During heating, the aqueous glycol solutions were deaerated with high purity (low oxygen) nitrogen gas or aerated with laboratory air. These gasses were passed through gas dispersion tubes immersed in the glycol solutions. The nitrogen gas line was equipped with a commercially-available oxygen trap to minimize oxygen entry into the deaerated reaction solutions. Deaeration was begun at least 60 h before heating began. To investigate the effects of metallic copper and aluminum on the glycol degradation, coupons ($19 \times 50 \times 0.8 \text{ mm}^3$) of these metals were placed in selected tubes. The coupons of 110 copper and 1100 aluminum alloys were placed in the test solutions immediately prior to heating.

The experimental details are summarized in table 1. Each reaction condition (temperature, present of metal and aeration/deaeration) was carried out in duplicate.

3.4. Measurement of acidic degradation products

For each determination of the concentrations of acidic degradation products, a 4–6 ml aliquot of the heated aqueous glycol solutions was removed from the reaction tubes. Each aliquot was placed in a stoppered vial and stored in a refrigerator at about 5°C . Before analysis, the vials were removed from the refrigerator, and allowed to warm to room temperature. Test solutions for ion-chromatography analysis were prepared by diluting 1 ml of the degraded glycol solution with 3 ml of distilled water. If the resulting solution was too concentrated and the limits of

Table 1
Summary of degradation conditions

Glycol	ethylene glycol; 1,2-propylene glycol (9 mol/l aqueous solutions)
Temperature	75, 86, 101°C
Metals used	none; 110 Cu alloy; 1100 Al alloy
Aeration condition	laboratory compressed air; low oxygen content nitrogen gas

detection of the ion-chromatograph were exceeded, the test solution was further diluted as necessary and re-analyzed.

Since the ion-chromatograph was equipped with an automatic sampler, analyses of the degraded glycol solutions were carried out in sets which consisted of approximately 20–25 test solutions. Calibration of the ion chromatograph, as previously described [7], was done before each set and after every 7th or 8th specimen during the set. Drift of the calibration was generally within $\pm 15\%$ of the initial calibration, although at times the drift was over 20%. The measured concentrations of the degradation products were adjusted for drifts in the chromatograph calibration.

For a given set of degradation conditions (temperature, presence of metal and aeration/deaeration), every second reaction point was analyzed twice using the ion chromatography procedure. It was not possible to analyze every sample twice because of the number of analyses to be undertaken. Duplicate readings of the concentrations of the acidic degradation products were generally found to be within 10% of the average. Readings differing by more than 10% were most often observed in cases where the degradation products were present in low concentrations (less than 10 ppm) or high concentrations (greater than 1000 ppm).

The aqueous glycol solutions heated at some temperatures in the presence of metallic copper and aluminum formed precipitates during the course of the degradation. Precipitates were observed in the following solutions at the noted times: ethylene glycol solutions heated at 86 and 101°C with copper after about 2650 and 550 h, respectively; ethylene glycol solution heated at 101°C with aluminum after about 3000 h; and propylene glycol solution heated at 101°C with copper after about 2000 h. The precipitates formed in the cylindrical reaction tubes could not be reproducibly sampled when aliquots of the glycol solutions were removed for analysis. Solutions having precipitates were centrifuged for 10 min at 1000 rpm, then separated from the centrifuged solids using an eye dropper, and finally filtered through a 0.2 μm pore filter. The resulting solution was analyzed using the ion chromatographic procedure.

During the course of the study, the ion chromatograph picked up a contaminant which had a retention time similar to that of oxalic acid. All attempts to eliminate the contaminant failed. The effect of the contaminant on the measured concentration of oxalate anions could not readily be accounted for through calibration procedures. Thus, oxalate anion concentrations are not reported in this paper. Estimates of the concentrations of oxalate present in the degraded glycol solutions were generally less than 20 ppm.

4. Results and discussion

The concentrations of glycolate and formate anions were determined for the ethylene glycol solutions. The concentrations of lactate, formate, and acetate were measured for the propylene glycol solutions. Figs. 1, 2 and 3 present the results of the measurements of these degradation products with time for aerated solutions at

75, 86 and 101°C, respectively. The plots in these figures were generated using a statistical and graphical data analysis software package entitled "Dataplot" [10]. The curves in these plots were obtained by using a robust curve smoothing technique incorporated in "Dataplot."

In each of the figs. 1, 2 and 3, the left column of plots represents the results for ethylene glycol, while the right column shows those for propylene glycol. Similarly, each row of plots in these figures shows the effect of the presence or absence of a

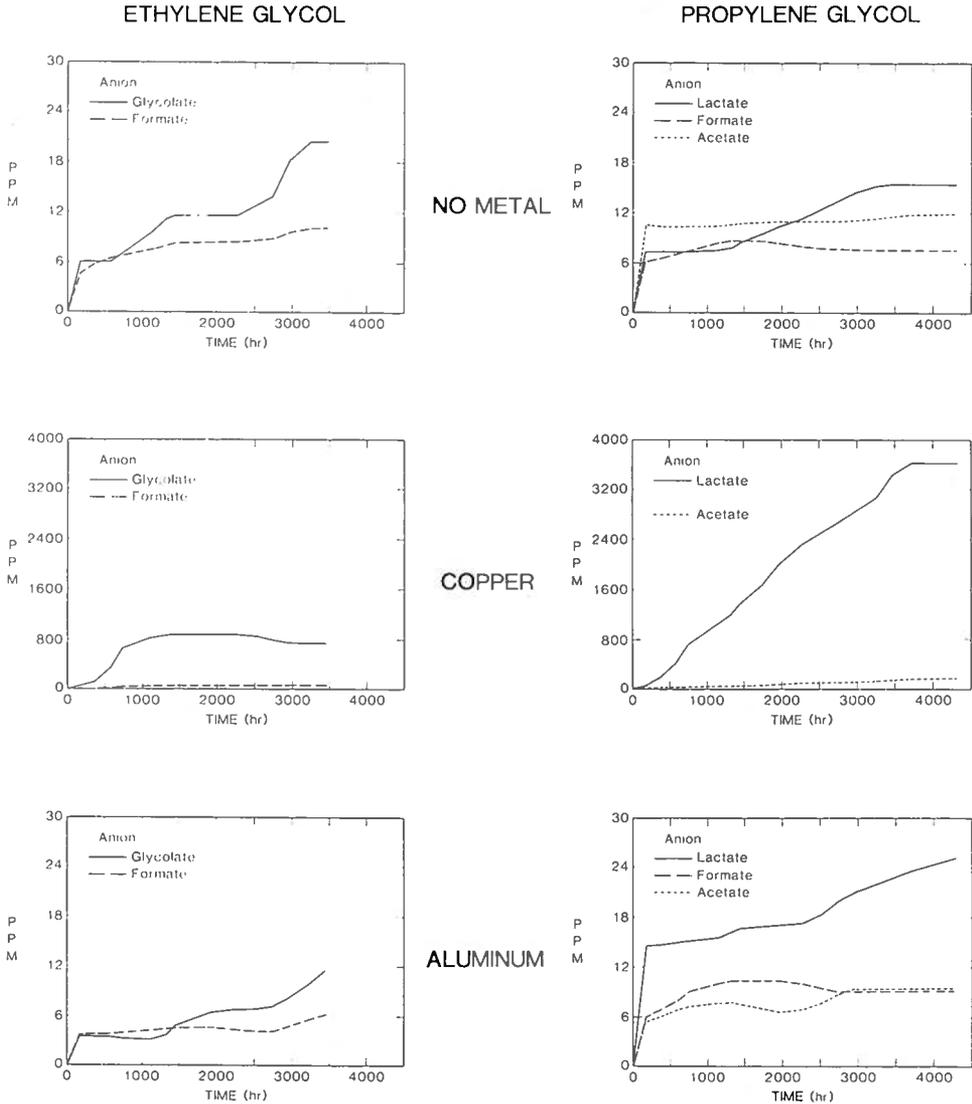


Fig. 1. Concentrations of degradation products in parts per million (ppm) as a function of time for aqueous aerated glycol solutions heated at 75°C.

metal: the top row is for degradation in the absence of metal; the middle row is for degradation in the presence of metallic copper; and the bottom row is for degradation in the presence of metallic aluminum.

4.1. Glycol effect

The results indicated that when heated in the absence of metal with aeration, little difference was observed in the amounts of degradation products formed from

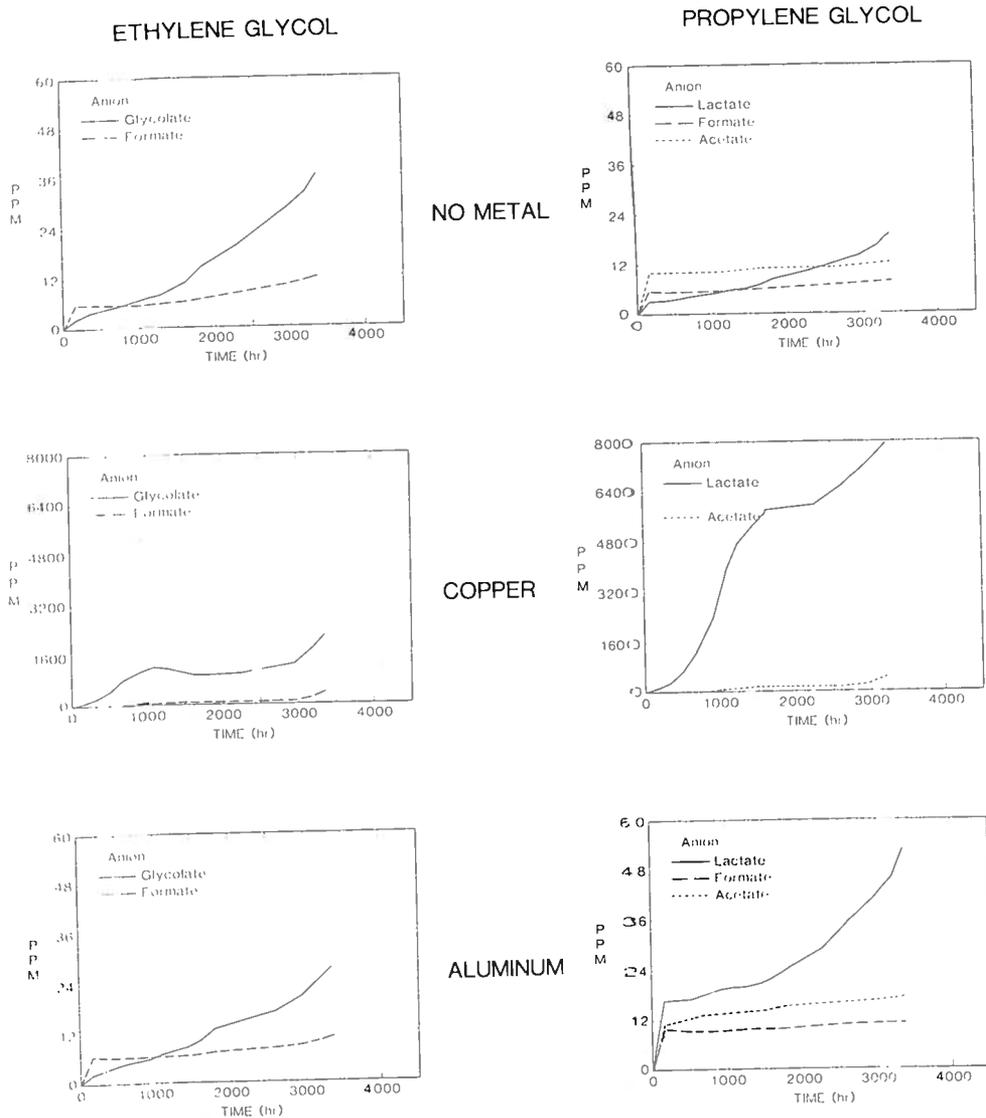


Fig. 2. Concentrations of degradation products in parts per million (ppm) as a function of time for aqueous aerated glycol solutions heated at 86°C.

ethylene and propylene glycol solutions. For example, at 86°C, the total concentration of degradation products in the ethylene glycol solution was about 40 ppm, while that in the propylene glycol solution was about 35 ppm (fig. 2). When aluminum was present, both types of glycol yielded comparable amounts of degradation products except at 101°C. At this temperature, after 2000 h of testing, propylene glycol yielded greater concentrations of degradation products than ethylene glycol. No comparison was made between the two glycols when copper was present because the

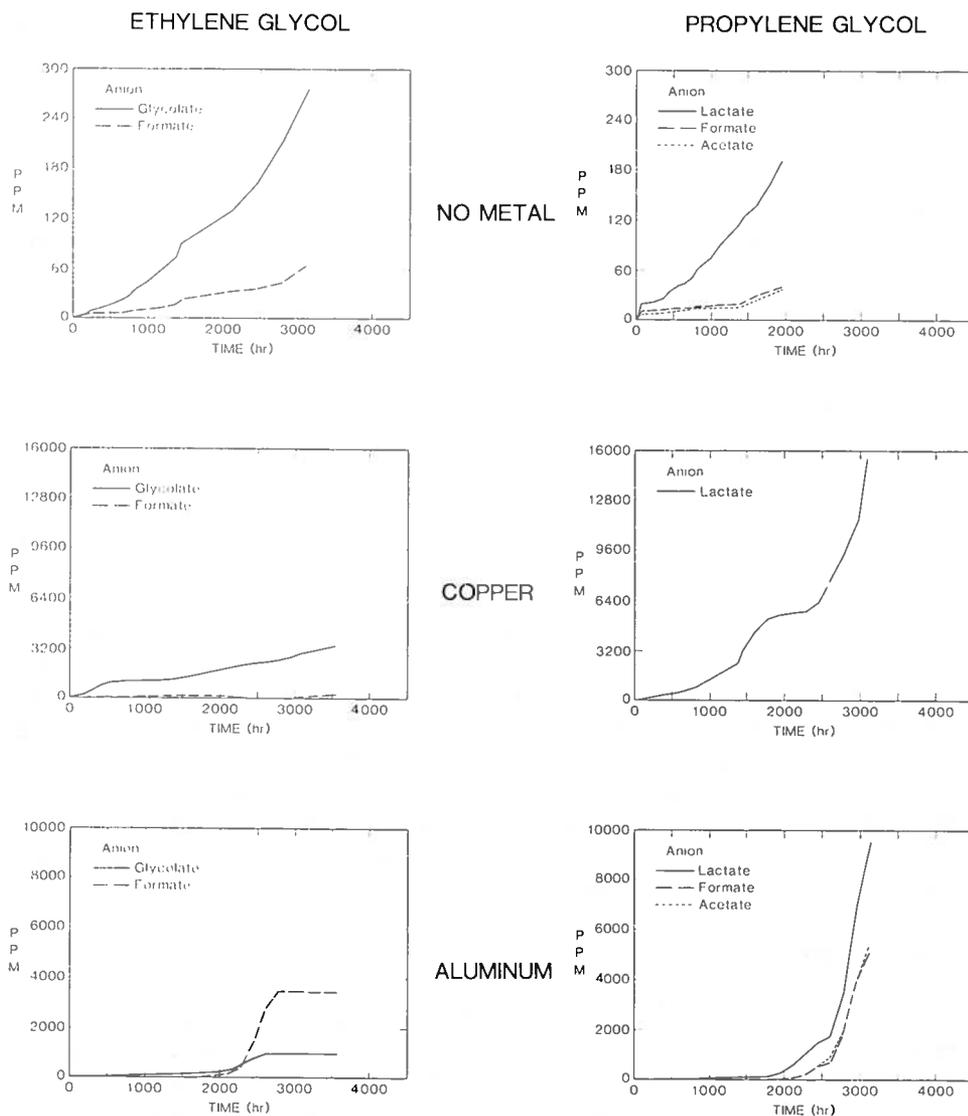


Fig. 3. Concentrations of degradation products in parts per million (ppm) as a function of time for aqueous aerated glycol solutions heated at 101°C.

contribution of the precipitates to the total degradation product could not be accounted for.

4.2. Temperature effect

As is evident by a comparison of the plots in figs. 1, 2 and 3, in the absence of metal with aeration, as the temperature of the degradation was increased, the amount of degradation product in solution in general increased. For example, for the aerated ethylene glycol solutions in the absence of metal, the maximum concentrations of degradation product in solution were about 23, 40 and 315 ppm for temperatures of 75, 86 and 101°C, respectively. At the same temperatures for the aerated propylene glycol solutions in the absence of metal, the concentrations of degradation product in solution were about 35, 35 and 260 ppm, respectively.

The greatest effect of temperature was observed in the case of propylene glycol solutions in the presence of aluminum. In this case, at 86°C, the concentration of lactate anion was about 50 ppm (fig. 2), while at 101°C it was near 10000 ppm (fig. 3). Reason for this exceedingly large increase in the amount of degradation with the increase in reaction temperature were not investigated. One possibility may be the presence of an oxidation accelerator.

4.3. Metal effect

It is clear from a comparison of figs. 1, 2 and 3 that copper metal had the most pronounced effect on the degradation of the glycol solutions. With the exception of both glycol solutions heated in the presence of aluminum at 101°C, the concentrations of degradation products found in the glycol solutions heated in the presence of copper were 1 to 2 orders of magnitude greater than those measured when the glycols were degraded in the absence of metal or in the presence of aluminum. The results of heating the glycol solutions in the presence of copper showed essentially one major degradation product [7]: ethylene glycol yields glycolic acid, while propylene glycol produces lactic acid. At 75 to 86°C the amounts of degradation products without metal or with aluminum present were comparable. However as previously indicated, at 101°C an effect of aluminum became apparent after about 2000 h of heating. The maximum concentrations of degradation products found in solution for both glycols heated in the presence of aluminum were similar to that produced in the presence of copper.

4.4. Deaeration effect

Fig. 4 presents the results of the analyses of degradation products in ethylene glycol and propylene glycol solutions heated at 75, 86 and 101°C with deaeration in the absence of metal. Since the degradation of the glycols is a thermal oxidative reaction [3,4], exclusion of oxygen should prevent degradation. As is evident in fig. 4, only a slight amount of degradation occurred. This was mainly attributed to some oxygen entering the reaction tubes when aliquots were being removed for analyses.

The concentrations of degradation products present were generally less than 50 ppm, even at 101°C. A temperature effect was not found for the deaeration experiments. For example, the three plots given in fig. 4 for ethylene glycol solutions at 75, 86 and 101°C have similar curves. A temperature effect would not have been expected, since the major factor influencing degradation in this case was contamination of the reactant solutions by oxygen.

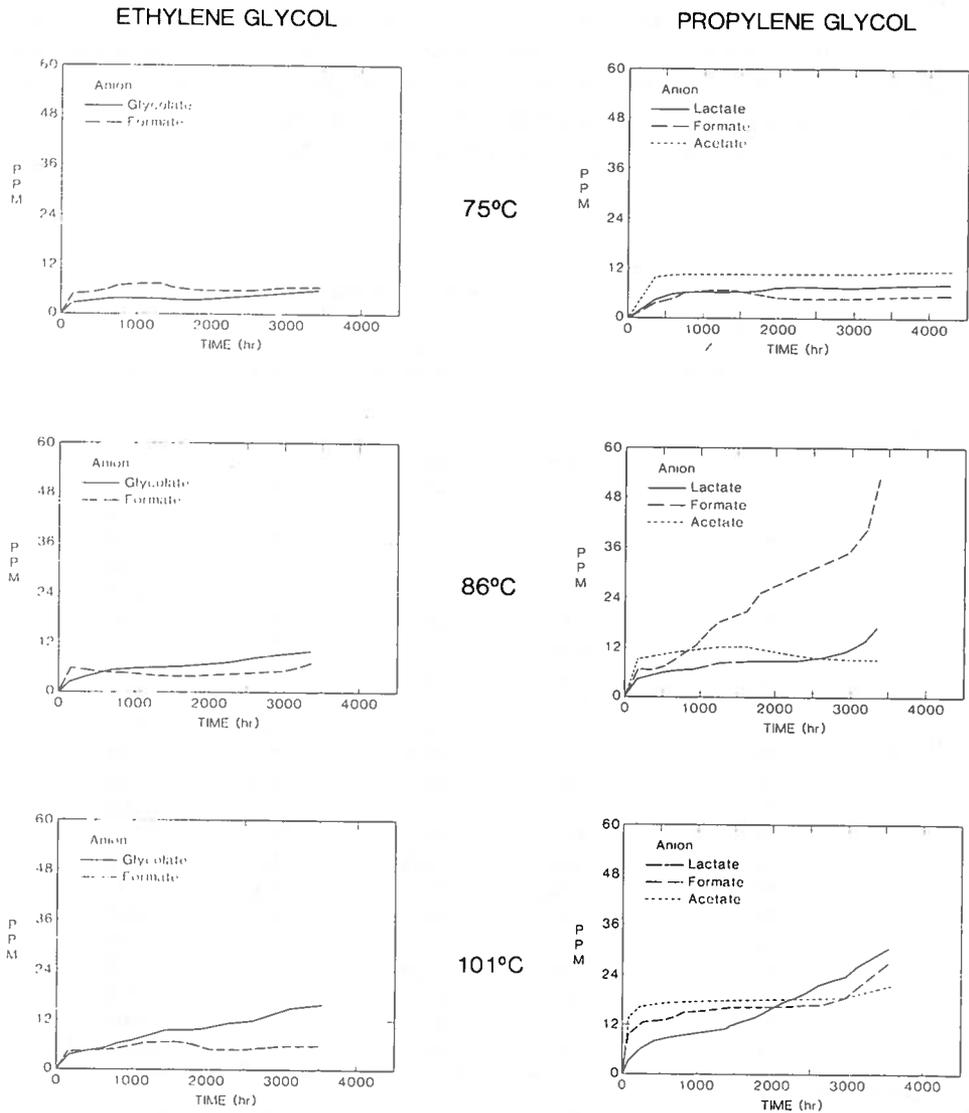


Fig. 4. Concentrations of degradation products in parts per million (ppm) as a function of time for deaerated glycol solutions heated at 75, 86 and 101°C.

4.5. The degradation of glycol solutions

In this study, the Ion Chromatography Exclusion (ICE) method of analysis was used to determine the concentrations of acidic degradation products formed in the thermal oxidation of aqueous ethylene and propylene glycol as influenced by time, temperature, the presence of metals and oxidative conditions. The thermal oxidative degradation of the glycols is a complex process, involving a free-radical mechanism [11]. The three major steps involve radical initiation, propagation and termination. Any factor which would alter the rate of any of these steps would have an effect on the overall rate of reaction. For example, initiators such as impurities which might be present in commercial collector systems would increase the rate of degradation. On the other hand, addition of inhibitors would be expected to reduce the rate of degradation and should be the subject of further investigation.

Table 2
pH values of the degraded glycol solutions and concentrations of degradation products

Glycol ¹⁾	Degradation condition ²⁾			Result		
	temperature (°C)	metal	aeration	pH	ppm ³⁾	
ethylene	75	none	N ₂ (g)	7.4	12	
	75	none	air	6.4	23	
	75	Cu	air	4.8	800	
	75	Al	air	6.7	14	
	86	none	N ₂ (g)	5.3	15	
	86	none	air	4.3	40	
	86	Cu	air	4.7	1400	
	86	Al	air	4.7	30	
	101	none	N ₂ (g)	2.0	20	
	101	none	air	2.3	315	
	101	Cu	air	3.6	2650	
	101	Al	air	3.6	2500	
	propylene	75	none	N ₂ (g)	7.4	24
		75	none	air	5.7	35
75		Cu	air	4.6	3000	
75		Al	air	6.1	39	
86		none	N ₂ (g)	6.6	58	
86		none	air	5.4	35	
86		Cu	air	4.1	7800	
86		Al	air	5.2	69	
101		none	N ₂ (g)	6.2	62	
101		none	air	4.0	260	
101		Cu	air	3.6	13000	
101		Al	air	3.6	16900	

¹⁾ 9 mol/l aqueous solutions.

²⁾ Data correspond to heating times of 3000 h except for aerated propylene glycol at 101°C without metal present. In this case the heating time was 2000 h.

³⁾ Total concentration of degradation products approximated from figs. 1, 2, 3 and 4.

Associated with the complexity of the degradation process is the fact that, in the presence of copper, essentially only one, but a different major degradation product, is formed from each glycol (figs. 1, 2 and 3). It is glycolic acid in ethylene glycol solution and lactic acid and propylene glycol solution. In the presence of aluminum, additional degradation products are found which may be produced from the further oxidation of glycolic acid and of lactic acid. Table 2 gives the total concentration of acidic degradation products for each reaction condition. A question not addressed in this study was whether copper retards the rate of glycolic and lactic acid degradation to prevent further oxidation, or whether additional degradation products are formed and then oxidized rapidly to carbon dioxide. It has been observed that carbon dioxide is produced during the thermal oxidation of aqueous ethylene glycol [12]. Finally, another factor which contributes to the complexity of these chemical systems is the formation of precipitates during the thermal oxidation in the presence of metals.

In view of the complexity of the thermal oxidation of aqueous ethylene glycol and propylene glycol solutions, it is considered to be impracticable in service to determine the extent of glycol degradation through an analysis of the degradation products. The analysis would involve at least the determination of concentrations of all acidic degradation products in solution, the amount of precipitate dispersed throughout the heat transfer system, and the amount of carbon dioxide produced. Other degradation products such as glycol polymers or esters produced from the reaction of the glycol with organic acid degradation products might also have to be analyzed.

A major concern affecting the use of aqueous glycol solutions as heat transfer fluids is that the decrease in solution pH, caused by the formation of organic acids during thermal oxidation, could accelerate the corrosion of metallic components of the collector system. The pH values of the solutions analyzed using the ICE technique have been determined [8]. Table 2 gives the pH values of these solutions as well as the maximum concentration of degradation products found in solution after heating for 3000 h, with the exception of aerated aqueous propylene glycol heated at 101°C for 2000 h in the absence of metal.

Results in table 2 indicate that all solutions underwent some degree of degradation, and became acidic. More importantly, however, these results in table 2 indicate that solutions which have undergone widely-varying amounts of thermal oxidation, as indicated by the concentration of degradation products, may have similar pH values. An example of this observation is given by the results for aerated propylene glycol solutions at 101°C. In this case, the concentrations of degradation products were found to be 260, 13000 and 16900 ppm without metal present, with copper present and with aluminum present, respectively. However, the respective pH values were 4.0, 3.6 and 3.6. The observation that the aqueous glycol solutions may have comparable pH values but considerably different concentrations of degradation products was attributed to the similar buffering range for the mixtures of weak organic acids and their conjugate bases formed by heating the glycol solutions in the presence of metallic copper or aluminum [7].

Since the data given in table 2 indicate that solutions with varying amounts of

degradation product may have similar pH values, monitoring the extent to which organic acid degradation products are formed cannot be used as an indicator of the potential corrosiveness of the solution. Since a decrease in pH is of importance, both the pH of the solution and the ability of the buffers to maintain the desired pH level should be monitored as has been recommended [3]. For initially unbuffered solutions, the results of the study have demonstrated that even a small amount of degradation product produces a decrease in pH of the solutions.

Another major concern associated with the use of aqueous glycol solutions is that the thermal oxidation will proceed to the extent that insufficient quantity of glycol will be available to provide freeze protection to the solar collector system. Thus, recommendations are often given to monitor the amount of glycol in the system by determining the solution density [3]. This recommendation is considered sound based on the results of this study. Degradation of the glycol solutions continues in time as indicated by the increase in degradation products (figs. 1, 2 and 3). Measurements of the pH values of the glycol solutions are not able to detect this continued degradation. Solution pH values in time become essentially constant when metals are present due to the buffering effect which develops as previously described [7].

Finally, although it may be obvious, the results of the investigation demonstrated that the exclusion of oxygen from the system is an effective means of reducing degradation. Only a small amount of degradation was observed in heating the deaerated solutions (fig. 4). Mechanistically, oxygen is needed for thermal oxidative degradation [11]. Closed solar collector systems from which oxygen is effectively excluded should provide longer service life of the glycol-based heat transfer fluids than those systems which constantly allow oxygen entry.

5. Summary and conclusions

This study investigated the thermal oxidative degradation of aqueous ethylene glycol and propylene glycol solutions. The concentrations of acidic degradation products were measured in time using the Ion Chromatography Exclusion (ICE) methods of analysis. Reactions were carried out with aeration at 75, 86 and 101°C in the presence of copper or aluminum, or in the absence of metal. Additional reactions were conducted without metal present and with deaeration at these temperatures. Based on the results of the study, the following conclusions were reached:

1. Acidic degradation products were produced under all reaction conditions.
2. Degradation was most extensive when copper metal was present in heated, aerated solutions.
3. At 75 and 86°C, the degradation of aerated glycol solutions with aluminum present was comparable to that of aerated glycol solutions in the absence of metal. At 101°C, degradation was significantly more extensive when aluminum was present, but this effect was not observed until after 2000 h of degradation.

4. The thermal oxidative degradation of aqueous glycol solutions is a complex process producing different reaction products in solution depending upon reaction conditions, in addition to precipitates and carbon dioxide. Monitoring the in-service stability of the glycol solution by the analysis of degradation products is not considered practicable, because of the complexity of the reaction.
5. There is no direct relation between the pH values of the degraded aqueous glycol solutions and the concentration of organic acid degradation products. The results of the study indicated that solutions having undergone relatively little degradation had pH values comparable to those which were more extensively degraded.
6. Although not unexpected, exclusion of oxygen from the system is an effective means of suppressing degradation since it is a thermal oxidative process.

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