

## CHARACTERIZATION OF POTENTIAL THERMAL DEGRADATION PRODUCTS FROM THE REACTIONS OF AQUEOUS ETHYLENE GLYCOL AND PROPYLENE GLYCOL SOLUTIONS WITH COPPER METAL

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Aqueous solutions of ethylene glycol and propylene glycol are common heat transfer fluids for solar collector systems. Thermal oxidative degradation produces organic acids which, in turn, generate copper salts through reaction with copper containment systems. Copper (II) salts of the organic acids which may be generated as the result of the degradation of the ethylene glycol and propylene glycol were prepared by reacting aqueous solutions of the acids with copper (II) carbonate. Infrared spectra and X-ray diffraction peak spacings and intensities are presented for the salts. These spectra may be useful in analyzing the service performance of heat transfer fluids used in solar collector systems.

### 1. Introduction

Aqueous solutions of ethylene glycol or propylene glycol are commonly used as heat transfer liquids in solar energy collection systems. Solar collectors and conduit are frequently fabricated from copper. Both ethylene glycol and propylene glycol are susceptible to thermal and thermal-oxidative reactions which generate organic acids. Copper (II) salts of these acids are, in turn, generated through reaction with copper containment systems.

The organic acids that may be generated in the thermal oxidative degradation of aqueous ethylene glycol and propylene glycol solutions are listed in table 1 [1-4]. Although there is little information on the composition of acidic degradation products formed in collector systems under field conditions, a recent laboratory investigation has identified the acids being formed under limited sets of experimental conditions [1,2]. These include glycolic, oxalic, formic, and carbonic acids from the degradation of ethylene glycol, and lactic, acetic, oxalic, and formic acids from the degradation of propylene glycol. In systems containing copper metal, the copper (II) salts of these acids may be formed. For example, in a previous laboratory study [1], precipitates, which were formed in the thermal oxidative degradation of aqueous ethylene glycol and propylene glycol solutions in the presence of metallic copper,

Table 1  
Potential acidic degradation products of ethylene and propylene glycols

| Ethylene glycol                              | Propylene glycol   |
|--|--|
| Glycolic acid ( $\text{HOCH}_2\text{COOH}$ ) | Lactic acid ( $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ ) |
| Glyoxylic acid ( $\text{HCOCOOH}$ )          | Pyruvic acid ( $\text{CH}_3\text{COCOOH}$ )                  |
| Formic acid ( $\text{HCOOH}$ )               | Formic acid  |
| Carbonic acid ( $\text{HOCOOH}$ )            | Carbonic acid  |
| Oxalic acid ( $\text{HOCCOOH}$ )             | Oxalic acid  |
|  | Acetic acid ( $\text{CH}_3\text{COOH}$ )                     |

were identified as copper (II) glycolate and copper (II) lactate dihydrate, respectively.

The infrared spectra and the X-ray diffraction spectra of many of the copper (II) salts of the acids in table 1 appear not to have been published. Accordingly, these spectra are reported to provide reference data for the analysis of the condition of heat transfer fluids in solar collector systems. The spectra are useful in the chemical identification of precipitates which may form in glycol solutions in service.

## 2. Experimental

Copper salts of the acids listed in table 1 were prepared by reacting aqueous solutions containing excess reagent grade acids with reagent grade copper (II) carbonate. Excess acid ( $\approx 20\%$ ) was used to assure complete reaction of the copper (II) carbonate. The reaction solutions were stirred at room temperature for 24 h during which time precipitates formed. The precipitates were then filtered, washed with distilled water, washed once with anhydrous methanol, and dried under a stream of nitrogen. After drying, the precipitates were ground using a mortar and pestle to approximately  $10\ \mu\text{m}$  particle diameter (obtained by micromesh screening). The reagent grade copper (II) carbonate was used in the as-received condition for infrared and X-ray analysis. Ion chromatograms of the solutions prepared from the copper (II) salts of glycolic and lactic acids were compared with those which resulted from the thermal oxidative degradation of ethylene or propylene glycol in the presence of copper metal [1]. Ion chromatographic analysis indicated identical retention times.

Specimens were prepared for X-ray diffraction in a manner to minimize preferred orientation. The X-ray spectra were obtained over a range of  $2\theta$  from  $6$  to  $66^\circ$ . The scanning rate was  $0.01^\circ\ 2\theta/\text{s}$ . Copper  $\text{K}\alpha$  radiation was used. Specimens were prepared for Fourier transform infrared (FTIR) spectroscopy by mixing the solid acid salts with KBr and pressing pellets. Transmission FTIR spectra were obtained over a range from 400 to 4000 wave numbers. All FTIR spectra were the result of 1000 co-additions and were taken at  $4\ \text{cm}^{-1}$  resolution. The FTIR sample chamber was purged with dry air for 5 min prior to scanning.

### 3. Results and discussion

Table 2 presents the results of the X-ray diffraction analyses and fig. 1 presents the infrared spectra of the copper (II) salts of the acids listed in table 1. Table 2 lists the interplanar spacing ( $D$ ) in Å and the normalized intensities ( $I$ ) for the 10 most intense diffraction peaks or for those having integrated intensities greater than 15%

Table 2

X-ray diffraction peak interplanar spacings ( $D$ ) and normalized integrated intensities ( $I$ ) for copper (II) salts of potential acidic degradation products of ethylene and propylene glycols

| Copper (II) glycolate |     | Copper (II) glyoxylate |     | Copper (II) oxalate           |     |
|-----------------------|-----|------------------------|-----|-------------------------------|-----|
| $D$                   | $I$ | $D$                    | $I$ | $D$                           | $I$ |
| 2.229                 | 100 | 2.397                  | 100 | 1.952                         | 100 |
| 5.66                  | 100 | 3.331                  | 100 | 3.904                         | 100 |
| 3.351                 | 61  | 5.13                   | 94  | 1.783                         | 25  |
| 4.78                  | 51  | 5.84                   | 74  | 1.768                         | 24  |
| 1.606                 | 39  | 3.235                  | 61  | 2.494                         | 20  |
| 1.436                 | 32  | 1.826                  | 55  | 1.952                         | 17  |
| 1.881                 | 31  | 2.827                  | 54  |                               |     |
| 2.503                 | 30  | 2.196                  | 48  |                               |     |
| 1.451                 | 30  | 2.924                  | 45  |                               |     |
| 2.229                 | 27  | 2.397                  | 44  |                               |     |
| 3.236                 | 25  | 2.435                  | 43  |                               |     |
| Copper (II) formate   |     | Copper (II) carbonate  |     | Copper (II) lactate dihydrate |     |
| $D$                   | $I$ | $D$                    | $I$ | $D$                           | $I$ |
| 5.21                  | 100 | 2.861                  | 100 | 11.48                         | 100 |
| 4.80                  | 88  | 3.685                  | 63  | 2.87                          | 36  |
| 3.065                 | 43  | 2.515                  | 60  | 3.368                         | 34  |
| 3.468                 | 37  | 1.421                  | 50  | 2.525                         | 30  |
| 3.229                 | 36  | 5.02                   | 45  | 2.132                         | 30  |
| 2.340                 | 34  | 1.590                  | 37  | 3.96                          | 27  |
| 2.075                 | 32  | 2.461                  | 35  | 3.704                         | 27  |
| 2.060                 | 31  | 1.478                  | 34  | 2.057                         | 27  |
| 2.482                 | 29  | 2.124                  | 32  | 1.692                         | 27  |
| 2.877                 | 28  | 1.673                  | 32  | 1.590                         | 27  |
| Copper (II) lactate   |     | Copper (II) pyruvate   |     | Copper (II) acetate           |     |
| $D$                   | $I$ | $D$                    | $I$ | $D$                           | $I$ |
| 7.35                  | 100 | 5.40                   | 100 | 6.90                          | 100 |
| 3.911                 | 73  | 4.36                   | 97  | 2.292                         | 74  |
| 5.24                  | 67  | 4.67                   | 54  | 3.527                         | 49  |
| 2.324                 | 24  | 2.702                  | 40  | 6.16                          | 38  |
| 3.329                 | 23  | 2.345                  | 38  | 3.587                         | 33  |
| 2.617                 | 17  | 2.144                  | 33  | 5.37                          | 27  |
| 2.635                 | 13  | 8.13                   | 30  | 5.86                          | 25  |
| 2.036                 | 12  | 2.175                  | 29  | 2.331                         | 24  |
| 2.371                 | 11  | 9.36                   | 28  | 1.966                         | 22  |
| 2.2058                | 10  | 1.717                  | 26  | 2.390                         | 20  |

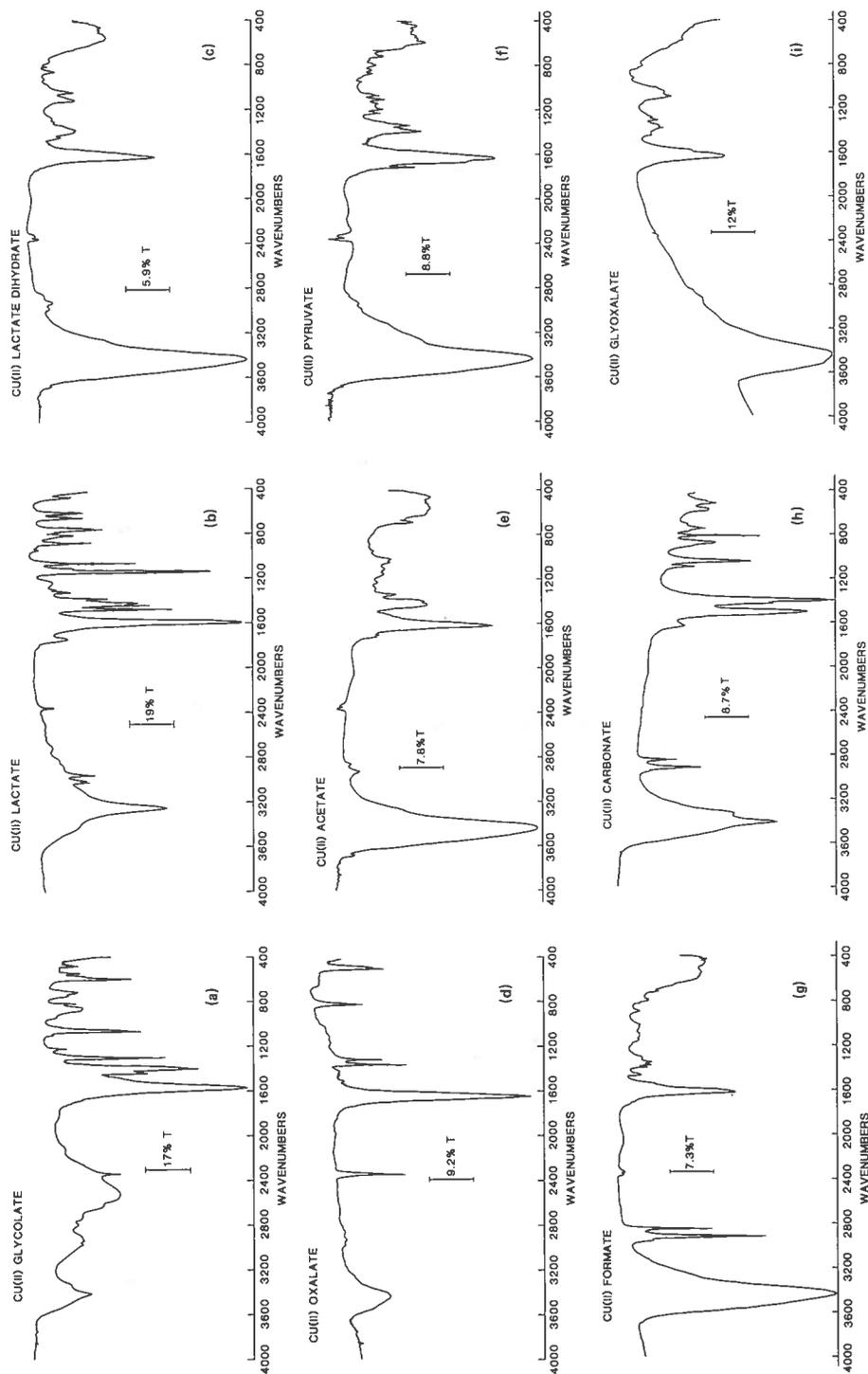


Fig. 1. Infrared spectra of copper (II) salts of potential acidic degradation products of ethylene and propylene glycols.

of the most intense peaks. The interplanar spacings listed were calibrated with respect to a quartz standard.

X-ray diffraction and infrared analyses were also performed on samples of copper (II) glycolate and copper (II) lactate obtained in previous investigations [1,5] in which aqueous ethylene glycol and propylene glycol solutions were degraded under simulated service conditions. The infrared spectrum of the copper (II) glycolate sample from the degradation of ethylene glycol was identical to that prepared in the present study. The X-ray diffraction spectra also showed excellent agreement. However, the infrared spectra of the two copper (II) lactate specimens were slightly different and the X-ray diffraction spectra were completely different. These differences were found to be related to differences in degree of hydration of the sample from the degradation of propylene glycol and that prepared in this study. It was found that anhydrous copper (II) lactate was prepared in the present study. When this anhydrous sample was allowed to equilibrate for 48 h in a desiccator over water, copper (II) lactate dihydrate formed. X-ray diffraction and infrared spectra of the dihydrated copper (II) lactate were in agreement with those of the sample obtained by thermally degrading propylene glycol.

#### **4. Summary**

Copper (II) salts were prepared from organic acids which may be produced as degradation products during the thermal oxidation of aqueous ethylene glycol and propylene glycol solutions. Infrared and X-ray diffraction spectra of the salts were reported. These spectra may be useful in analyzing the service performance of heat transfer fluids used in solar collector systems.

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