

CORROSION INHIBITION OF COPPER IN CONTAMINATED ALCOHOLS

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ABSTRACT

The inhibitive action of benzothiazole (BTA) and benzimidazole (BIZ) in alcohols contaminated with methanoic and ethanoic acids was studied by gravimetric and galvanostatic polarization techniques. Alcohols in pure state are non-corrosive and the presence of contaminants such as water, methanoic and ethanoic acids stimulates corrosion. Methanoic acid caused rapid corrosion of copper than ethanoic acid due to its relative acid strength. Results showed that both BTA and BIZ formed compact protective films of cuprous complex - Cu (BTA)_n and/or Cu (BIZ)_n which was readily adsorbed on the metal surface. The higher inhibition efficiency values of BTA appeared to be due to insolubility of Cu(BTA)_n complex.

KEYWORDS: Inhibition, alcohols, copper, BTA, BIZ

INTRODUCTION

Alcohols are of increasing interest as fuel substitutes for coal, oil and/or natural gas (Menrad and Konig, 1982). Alcohols can be derived from renewable energy sources, such as biomass, in conjunction with solar power. Thus in order to check global pollution problems resulting from conventional energy production and use, secondary energy carriers based on alcohol will be of increasing importance.

These days a large number of Brazilian vehicles run on ethanol rather than a conventional hydrocarbon fuels (Finguern, 1998). New uses for lower alcohols are being discussed in several fields (C.E.C., 2005 and Wikipedia, 2005). One of such is the application of methanol as an "additive" to process streams during offshore oil and gas production. Methanol inhibits formation of hydrocarbon gas hydrate deposits (Kopp and Kopp, 1981). Another proposal is based on the use of methanol as a carrier fluid for coal slurry transport in pipelines.

Owing to chemical differences between hydrocarbon fuel and alcohol, corrosion problems are intrinsically more severe with alcohols. Hydrocarbon fuels are not miscible with water, nor do they dissolve corrosive inorganic materials. For this reason, corrosion is a minor problem with these fuels (Trabenalli and Carassati, 1970). On the other hand, alcohol dissolves both water and inorganic salts. Some practical methanol and ethanol fuels have been found to contain appreciable amounts of formic and ethanoic acids respectively (Kopp and Kopp, 1981). It seems plausible that these acids are introduced by the production process or represent products of partial oxidation of the alcohols, although specific chemical oxidation mechanisms for such oxidation remain unknown. Representative values are 0.2% H₂O and 2mg/L methanoic acid in methanol, and 5% H₂O and 15mg/L ethanoic acid in methanol (Johnnie and Schenborn, 1985). These concentrations can cause severe corrosion of automotive parts. For example, fuel injection systems made from Cu and Cu alloys, or Al and Al alloys are attacked by fuel methanol (Menrad and Kenig, 1982).

The water content of alcohol fuel plays a significant role in metal corrosion. It is remarkable that minimum corrosion rates are found at specific water concentrations (Heltz, 1974). Moreso, the physical and chemical properties of alcohols influence corrosion. Specifically, the length of the aliphatic chain seems to afford corrosion protections. For this

reason, materials corrode more readily in methanol than in ethanol (Heltz 1974).

The aim of the present work was to examine the corrosion of copper in methanol and ethanol both in pure liquids and in alcohol solutions of HCOOH and CH₃COOH, CH₃COONa and HCOONa. This work was initiated in order to obtain deeper insight into the impact of such contaminants on corrosion in alcohols and to find out the inhibitive effect of BTA and BIZ in such solutions.

MATERIALS AND METHOD

Experiments were carried out with copper rods and plates (92.5% Cu, 7.5% Zn). The specimens were ground with emery paper up to 100 grades and rinsed with distilled water, and degreased with acetone and dried before immersion in test solutions. Analytical reagent grades of methanol (5% H₂O) Ethanol (5% H₂O), formic acid, acetic acid, BTA and BIZ were used without further purification.

Weight loss measurements were made after 12, 24, 36 and 48h immersion. Corrosion rates were determined by taking the average of triplicate weight-loss measurements. Rates at intermediate times were compared with the rate obtained for specimens immersed continuously for 48h at the temperature of 50°C. Uniformity in temperature was maintained by using a water circulating thermostat.

The Electrochemical measuring equipment was as described in Singh and Adeyemi, 1989. The electrochemical cell was modified to include a mechanical stirrer (designed in-house) to allow elimination of high ohmic voltage drop due to low solution conductivities ($X = 10^{-6}$ to 10^{-5} scm⁻¹). Polarisation measurements were commenced after four hour immersion in test-solutions (Pierre, 2004). Fresh solutions were prepared for cathodic and anodic curves. Galvanostatic measurements were made (point by point) after a quasi-steady state had been obtained at each voltage.

RESULTS AND DISCUSSION

Corrosion rates of copper are low in most cases in alcohol. They show one important peculiarity; the corrosion rate decreased with time in acidified ethanol solutions while they increased with time in acidified methanol. Copper corrosion increased distinctly upon addition of corresponding acids but a maximum weight loss of 0.3mpy⁻¹ with CH₃COOH addition (figure 1) might qualify copper as a relatively resistant material. Copper corrosion rates increased with temperature (Table 1) in acidified solutions. The average weight loss was as much as 0.4 mpy⁻¹.

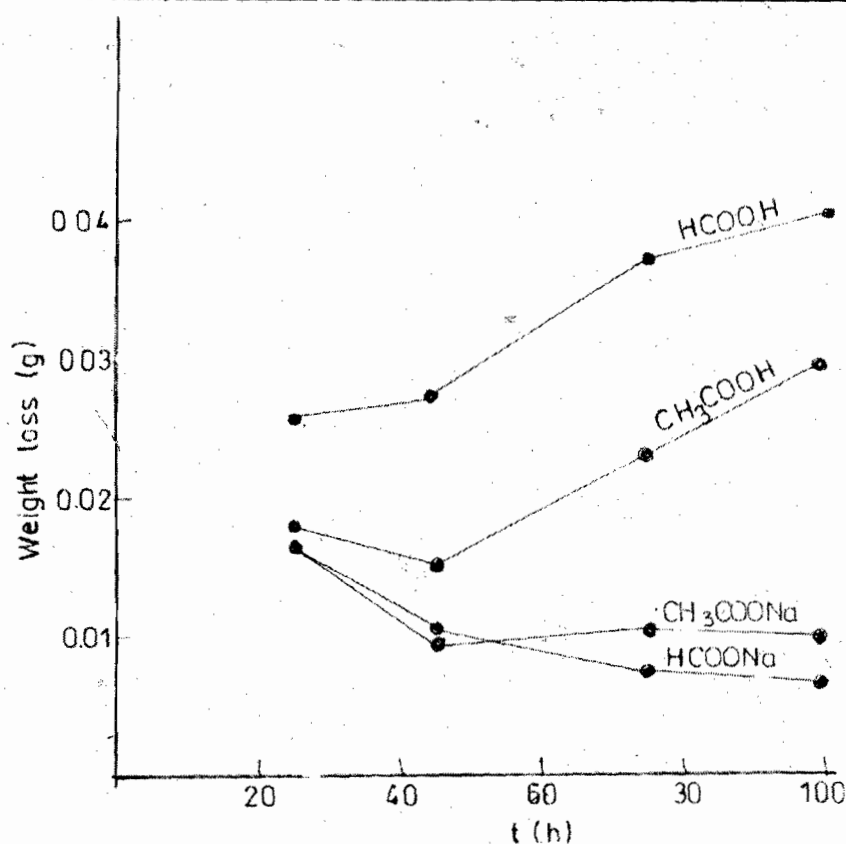


Fig. 1: Time dependence of Cu weight loss in C_2H_5OH solutions of 0.1M CH_3COOH , $HCOOH$, CH_3COONa , $HCOONa$

Table 1: Weight loss rates ($gm^{-2}h^{-1}$) of Cu in alcohols in the presence of additives

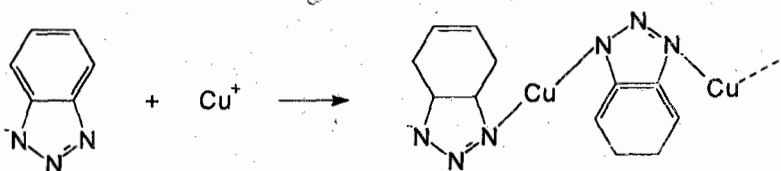
Concentration ($mol\ l^{-1}$)	Weight Loss ($gm^{-2}h^{-1}$)	
	CH_3OH	C_2H_5OH
Without contamination	0	0
CH_3COONa		
0.1M	0	0
CH_3COOH		
0.1M	0.03	0.18
$HCOONa$		
0.1M	0.01	0.00
$HCOOH$		
0.1M	1.66	2.27
0.05M	1.64	1.76
0.01M	0.83	0.59

The addition of inhibitors produced significant effect as evidenced from (Table 2). The higher efficiency values exhibited by BTA were assumed to be due to formation of an insoluble protective film of complex polymer on the copper

surface. Spectrometric studies (Heakal and Haryama, 1986; Mansikkamaki, et al, 2005) on the protective film of BTA have proposed a chain structure of the complex polymer formed by the reaction of copper ion with BTA as

Table 2: Inhibition percent (%) in the presence of BIZ and Benzothiazole (BTA) benzoimidazole.

Concentration ($mol\ l^{-1}$)	0.1M BIZ		0.1M BTA	
	CH_3OH	C_2H_5OH	CH_3OH	C_2H_5OH
CH_3COOH				
0.1M	85.23	87.75	96.67	96.85
$HCOONa$				
0.1M	86.05	86.05	97.05	96.85
$HCOOH$				
0.1M	86.45	86.62	97.65	97.70
0.05M	86.73	86.75	97.73	97.33
0.01M	86.77	86.78	97.76	97.59



Variation in Cu corrosion rates with different inhibitors demonstrated the influence of individual inhibitors employed. The larger weight loss in the absence of inhibitors

is corroborated by polarization curves (Figures 2 and 3). The intersection of the two hypothetical Tafel slopes occurs at lower current densities with inhibitors than without.

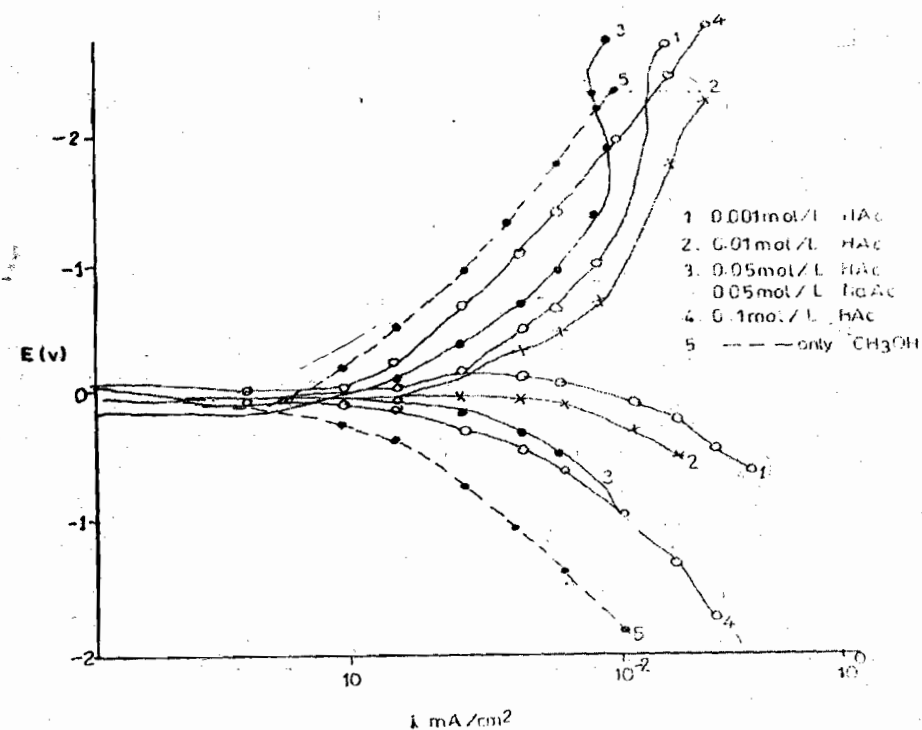


Fig. 2: Polarization curves of Cu in CH₃OH solutions of CH₃COOH/HCOONa

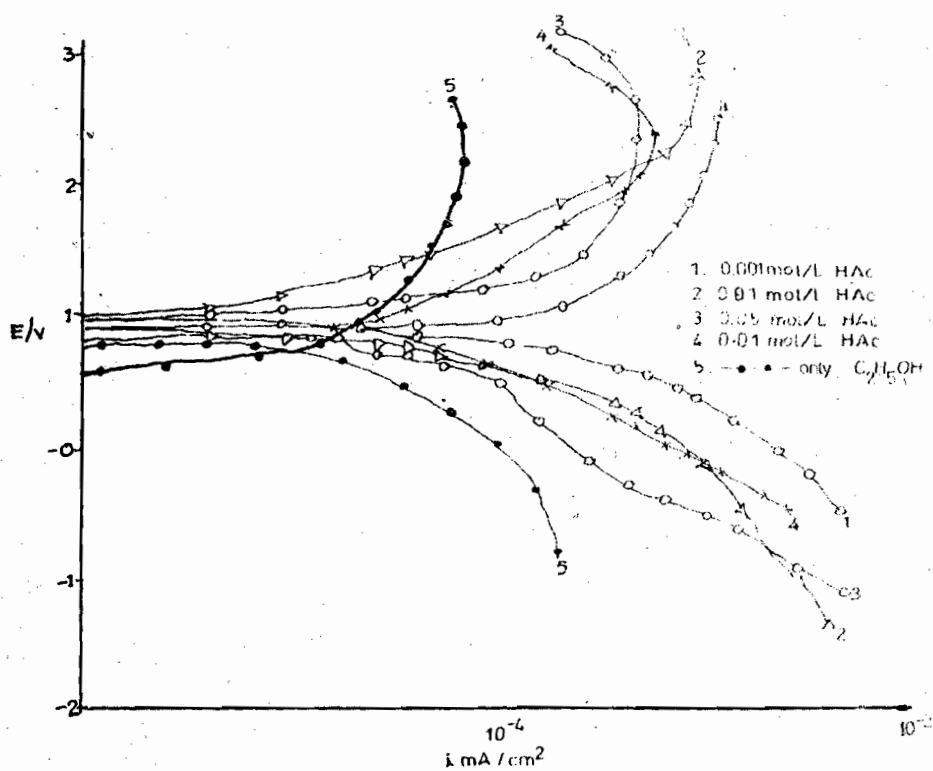


Fig. 3: Polarization curves of Cu in C₂H₅OH solutions of CH₃COOH/CH₃COONa

Neither the cathodic nor the anodic branch was found to exhibit any distinct gradation due to pH and visual inspection of the Copper specimens in pure methanol showed no gas evolution in the anodic or cathodic region. Upon the addition of 0.1M CH₃COOH only a few gas bubbles were observed on the working electrode. At positive potentials, no gas was generated at the counter electrode. The shapes of the polarization curves were similar owing to the lower solvent conductivity. The working electrode dissolved under anodic load while the platinum (Pt) counter electrode was covered with copper, and the solution turned blue. A milky precipitate possibly of Cu (OC₂H₅)₂ or Cu(OCH₃)₂ appeared at pH 9. A potential decrease was observed only in methanol and in its 0.1M CH₃COOH solutions. Alcoholic solutions exhibited well defined tafel slopes fig. 3.

Because of their relative acid strengths, formic acid caused more rapid corrosion than acetic acid. The corrosion rates exhibited a non linear dependence upon HCOOH and CH₃COOH addition. With the exception of Cu/CH₃OH, the corrosion rate decreased with time. Addition of inhibitors retarded the corrosion rate of copper in contaminated alcohol solutions. BTA is more effective due to the relative stability of its complex polymer on copper surface. Polarization curves are generally insensitive to explain the parameter variations summarized above. Extrapolated Tafel plots gave qualitative agreement with weight-loss measurements.

CONCLUSION

The parameterization study of copper corrosion in non aqueous alcohols illustrates that alcohols in pure state are non-corrosive to copper but becomes corrosive in the presences of contaminants such as water, formic and acetic acids respectively.

The present studies show that presence of formic and acetic acids in alcohols stimulates corrosion and corrosion is more rapid in the presence of formic acid than acetic acid due to their relative acid strengths.

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