Inhibition studies in sweet corrosion systems by a quaternary ammonium compound

R. ZVAUYA*, J. L. DAWSON‡

Corrosion and Protection Centre, University of Manchester Institute of Science and Technology, Manchester, M60 1QD, Great Britain

Received 16 August 1993; revised 23 December 1993

Benzyl dimethyl-n-hexadecylammonium chloride (BHDC) was investigated for its effectiveness as a corrosion inhibitor of pure iron in carbon dioxide saturated 3% sodium chloride solutions. Both a.c. impedance and d.c. electrochemical techniques were used. The compound inhibited the anodic reaction and was effective at low temperatures. Data obtained fitted the Frumkin adsorption isotherm. The inhibition characteristics are interpreted in terms of thermodynamics and the structure of the compound.

1. Introduction

Most research concerned with fundamental principles of corrosion inhibition has been done in either hydrochloric acid or hydrogen sulphide aggressive solutions [1-4]. Most work on carbon dioxide corrosion inhibition studies is concerned with commercial preparations [5]. There is little literature on fundamental studies of inhibition in CO2 systems. Such studies are important for the design of organic inhibitors used in industrial applications.

The adsorption of inhibitor molecules from an aqueous solution can be regarded as a quasisubstitution process between the organic compound in the aqueous phase org(aq) and water molecules adsorbed at the electrode surface, \( \mathrm{H_2O(s)} \):

\[
\mu \mathrm{Org(aq)} + x \mu \mathrm{H_2O(s)} = \mu \mathrm{Org(s)} + x \mu \mathrm{H_2O} \quad (1)
\]

where \( x \), the size ratio, is the number of water molecules displaced by one molecule of organic inhibitor, \( \mathrm{org(aq)} \), is a molecule of the inhibitor and \( \mu \) is the chemical potential. There is a complex relationship between electrode corrosion kinetics, organic inhibitor structure, and adsorption of the organic compound.

The present study was carried out in 3% sodium chloride solutions saturated with carbon dioxide at low temperatures and atmospheric pressure using pure iron. It has been shown that this system is under cathodic kinetic control during corrosion of iron [6]. The compound benzyl dimethyl-n-hexadecylammonium chloride (BHDC) was used as an inhibitor of iron corrosion in brine saturated with carbon dioxide. BHDC is a quaternary ammonium salt, has a benzene ring and a long alkyl chain, all of which factors play a part in its role as an inhibitor. The structure of the compound is:

Both d.c. techniques and electrochemical impedance were used. The results are interpreted in terms of chemical thermodynamics and the molecular structure.

2. Methods

The measurements were carried out in 3% sodium chloride solutions saturated with carbon dioxide. The solutions were deaerated by purging with nitrogen (oxygen free) continuously for 4h. The electrodes were made of 99.999% pure iron rods (Johnson Matthey) cast in Araldite. The working electrode was polished on 800 grade emery paper and degreased with ethanol before measurements.

The polarization measurements were made using a Wenking potentiostat (LT 78) and a three electrode arrangement consisting of a platinum counter electrode and a saturated calomel reference electrode (SCE). The electrode potential was allowed to reach steady state, which took about 50 min. The electrode was then polarized in 20mV steps, waiting 1 min at each step to allow the potential to reach steady state. At a cathodic potential of \(-1000\) mV vs SCE the cathodic current was stopped and the electrode allowed to return to the rest potential. The anodic portion was then obtained in 10mV steps, waiting...
I min at each step. The procedure was repeated with inhibitors. Electrochemical impedance measurements were carried out with a Solartron 1174 transfer function analyser (TFA) using a digital technique of wave generation. The analyser was controlled by a desktop Hewlett Packard 85 computer. The TFA was programmed to sweep from a maximum frequency of 10 kHz to a minimum frequency of 100 mHz in seven steps per decade.

3. Results and discussion

The effect of adding benzyl dimethyl-hexadecylammonium chloride (BHDC) on the polarization curves is shown in Fig. 1. BHDC mainly inhibits the anodic reaction and raises the corrosion potential in the cathodic direction. However, the compound does not alter the Tafel slopes, indicating that the dissolution mechanism does not alter. The corrosion rate decreases with increase in inhibitor concentration.

Typical impedance plots obtained on addition of BHDC are shown in Fig. 2. All the impedance plots obtained were essentially semicircular, indicating that charge transfer is the controlling dissolution mechanism. The value of $1/R_t$ is proportional to the corrosion rate according to theory [1, 7, 8]. The