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Inhibition studies in sweet corrosion systems by a quaternary ammonium compound

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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

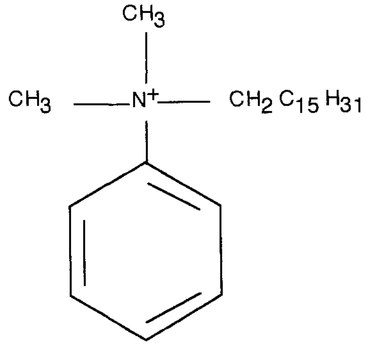
Most research concerned with fundamental principles of corrosion inhibition has been done in either hydrochloric acid or hydrogen sulphide aggressive solutions [1–4]. Most work on carbon dioxide corrosion inhibition studies is concerned with commercial preparations [5]. There is little literature on fundamental studies of inhibition in CO_2 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, $H_2O(s)$:

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

where x, the size ratio, is the number of water molecules displaced by one molecule of organic inhibitor, org(aq), is a molecule of the inhibitor and μ 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 dearated by purging with nitrogen (oxygen free) continuously for 4 h. 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 20 mV 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 10 mV steps, waiting

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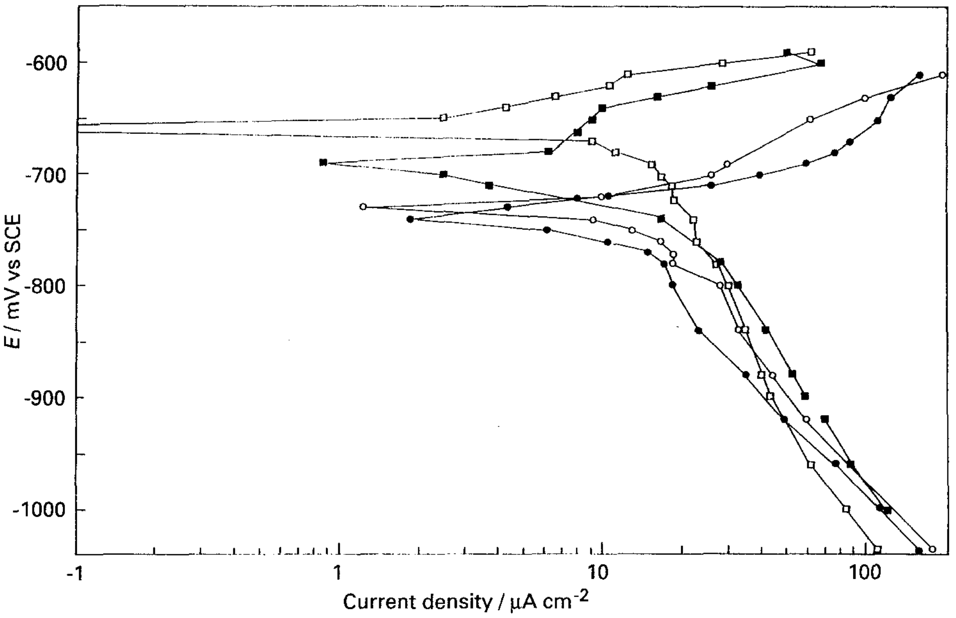

Fig. 1. Effect of increasing the concentration of benzyl dimethyl-*n*-hexadecylammonium chloride on the polarization behaviour of pure iron in CO_2 saturated brine solutions. (●) blank; (○) 0.10, (■) 0.50 and (□) 0.60 μM.

1 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

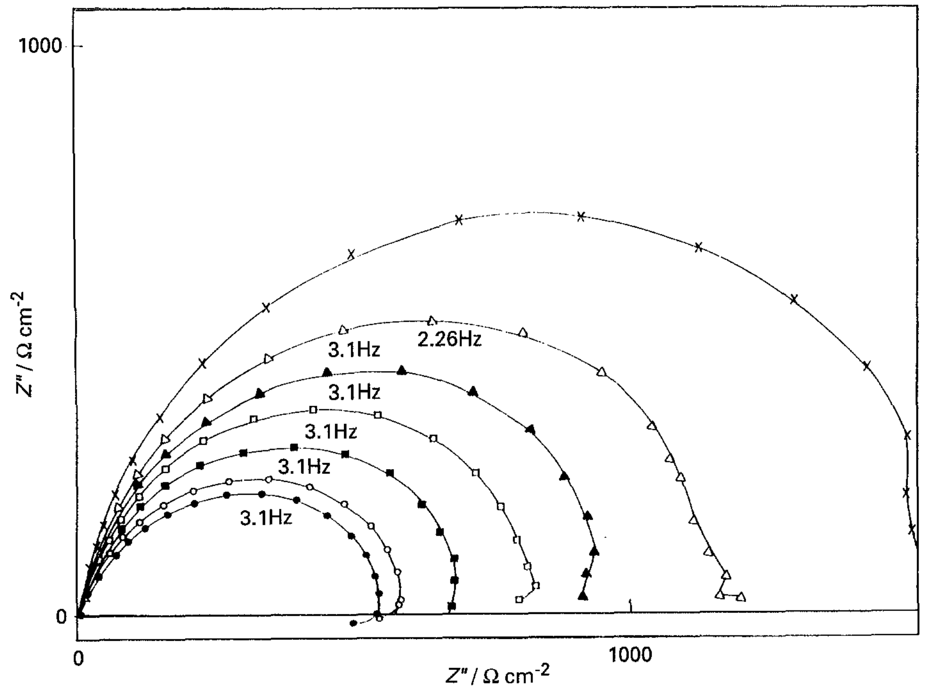

Fig. 2. A.c. impedance plots obtained at different concentrations of benzyl dimethyl-*n*-hexadecylammonium chloride using pure iron electrodes in CO_2 saturated brine solutions. (●) blank; (○) 0.10, (■) 0.20, (□) 0.30, (▲) 0.40, (△) 0.60 and (×) 0.80 μM.

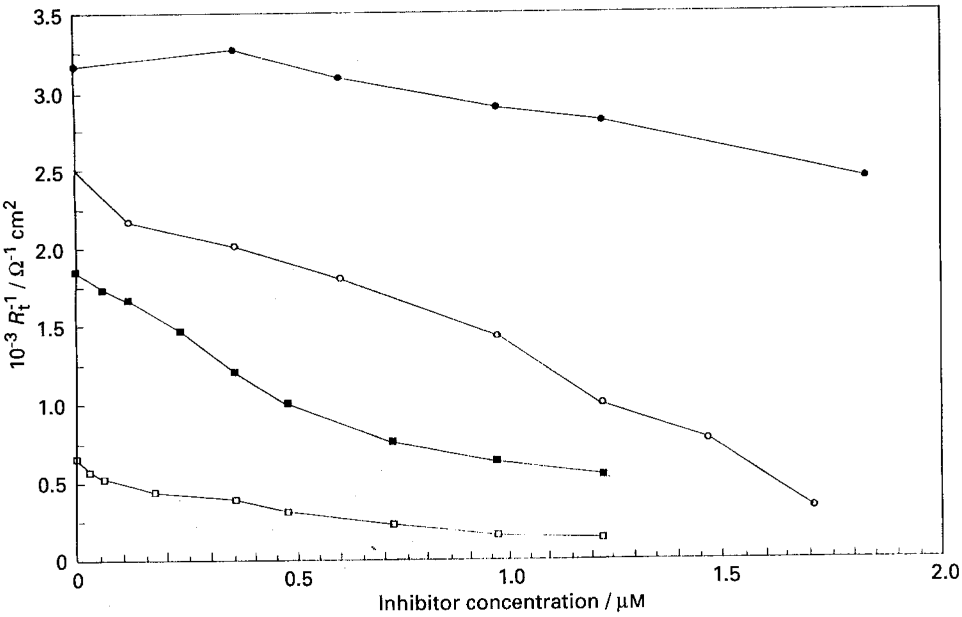

Fig. 3. Change in corrosion rate ($1/R_t$), with increrasing inhibitor concentration at various temperatures for pure iron in CO_2 saturated brine solutions: (□) 30, (■) 40, (○) 50 and (●) 60° C.

addition of the compound increases the charge transfer resistance, R_t, value i.e. the corrosion rate decreases.

The corrosion rates also increase with temperature as shown in Fig. 3. Thus, increasing the temperature from 30° C to 60° C increases the corrosion rate by a factor of five. The results show that the inhibitor is not very effective at high temperatures. Thus at 60° C an efficiency of 30% was obtained with the same inhibitor concentration that gave an efficiency of 70% at 30° C. The degree of surface coverage in most inhibitor studies is represented by percentage inhibitor efficiency which is calculated as follows:

$$\theta = \frac{i_b - i_c}{i_b} \qquad (2)$$

where i_b is the corrosion rate in uninhibited solution, i_c is the corrosion rate in inhibited solution and θ the degree of surface coverage.

Percentage inhibitor efficiency, P, is given by

$$P = \frac{i_b - i_c}{i_b} \times 100 \qquad (3)$$

Most experimental data on inhibition studies can be expressed in terms of the Frumkin isotherm which can be written as [9]

$$\frac{\theta}{1-\theta}\exp(-2a\theta) = \frac{C}{55.5}\exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (4)$$

$$= K^{*}C \qquad (5)$$

where C is the concentration of the inhibitor, θ the degree of surface coverage and a the molecular interaction constant. Also,

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (6)$$

The Frumkin adsorption isotherm is a general equation from which both the Langumuir and Temkin isotherms can be obtained as special cases. If no lateral interaction is assumed, then $a = 0$ and the Langumuir isotherm is obtained. If on the other hand there are strong repulsive forces then $a > 0$ and the Temkin isotherm is obtained:

$$\exp(-2a\theta) = KC \qquad (7)$$

However, the above expressions do not take into account x, the number of water molecules displaced. When this is taken into account then the relationship becomes the Bockris–Swinkels isotherm [10].

$$\left[\frac{\theta}{(1-X)^{x}}[\theta + X(1-\theta)^{(x-1)}]\right]/X^{x} = K^{*}C \qquad (8)$$

All the above isotherms can be expressed in the general form below:

$$f(\theta, x)\exp(-a\theta) = K^{*}C \qquad (9)$$

The free energy of adsorption can then be calculated from Equation 4. The above adsorption isotherms have a characteristic S-shape. In the intermediate range of surface coverage, 0.2 to 0.8, a linear dependence of θ against $\log C$ is obtained if $\log(\theta/(1-\theta))$ is neglected.

The values of a and K were calculated by choosing values of θ in the range 0.2 to 0.8 and the corresponding value of C. The two simultaneous equations were then solved. The values of K and a were entered into a computer programme which simulated the adsorption isotherms. The data fitted the Frumkin isotherm. Other thermodynamic quantities can also be calculated from Equation 10:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \qquad (10)$$

where H°_{ads} is the enthalpy of adsorption and S°_{ads} the entropy of adsorption.

A plot of free energy of adsorption against

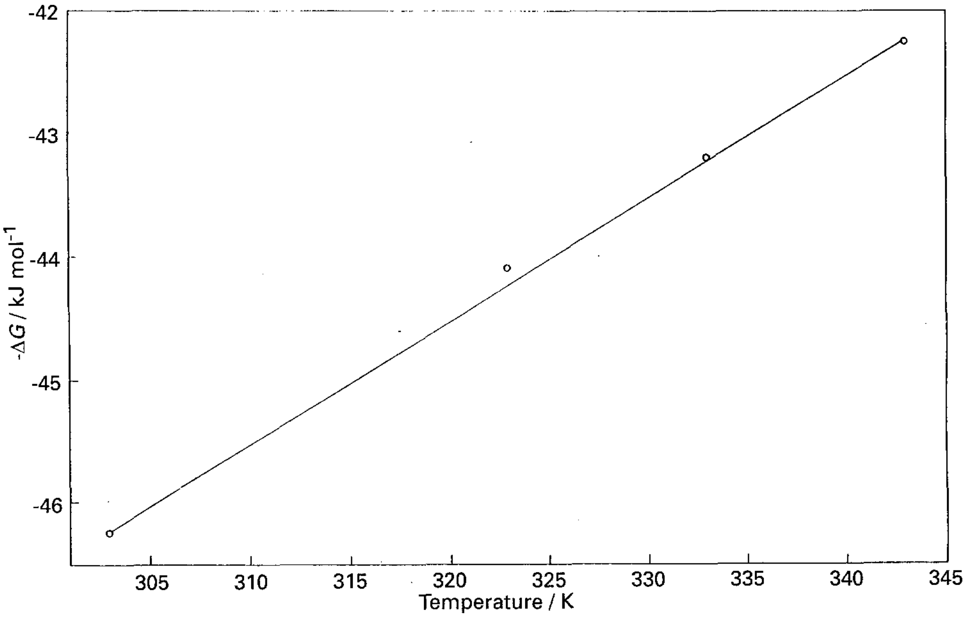

Fig. 4. Plot of free energy of adsorption against temperature for benzyl dimethyl-*n*-hexadecylammonium chloride.

temperature gave a straight line as shown in Fig. 4, from which other thermodynamic quantities were calculated. Plots of the Frumkin adsorption isotherm at various temperatures are shown in Fig. 5. The values of the thermodynamic quantities obtained are shown in Table 1.

BHDC has two possible reaction centres i.e. the positively charged nitrogen atom and the π electrons of the benzene ring. There are three possible orientations of the compound at the electrode surface. These are: (i) the perpendicular orientation with the alkyl chain protruding into solution, (ii) horizontal orientation with methyl groups protruding into solution, and (iii) the horizontal orientation with one of the methyl groups protruding into the solution.

The surface areas obtained from molecular models for the horizontal arrangements (ii) and (iii) are 85 Å^2 and 98 Å^2, respectively, which gives an x value of 9 or 10 if we consider that each molecule of water occupies 10 Å^2. On the other hand the perpendicular arrangement gives a surface area value 48 Å^2 and hence an x value of 5.

In the perpendicular orientation the molecule can be adsorbed both via the nitrogen atom and the π electrons of the benzene ring [11]. Furthermore, the formation of a close-packed layer in this orientation is made possible by the attractive forces between the negatively charged benzene ring on one molecule and slightly positively charged methyl groups on adjacent molecules. This, together with van der Waals forces of cohesion between long alkyl groups, results in attractive forces existing between adjacent

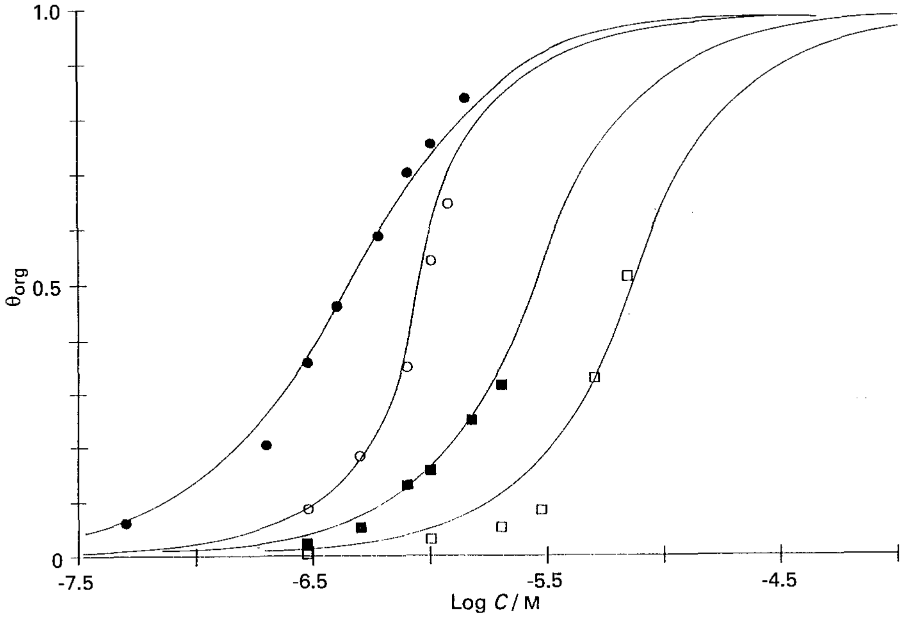

Fig. 5. Plot of the Frumkin adsorption isotherm for benzyl dimethyl-*n*-hexadecylammonium chloride at various temperatures: (●) 40, (○) 50, (■) 60 and (□) 70° C. (—) Simulation.

Table 1. Thermodynamic data for benzyl dimethyl-n-hexa decyl-ammonium chloride

ΔG^0_{ads} $/kJ\,mol^{-1}$	ΔS^0_{ads} $/JK^{-1}\,mol^{-1}$	ΔH^0_{ads} $/kJ\,mol^{-1}$	K*	a^*
−46.3	−117.6	−10.6	1 750 000	−1

* Constants in Frumkin isotherm.

adsorbed molecules [11]. This is in agreement with the *a* value obtained from the adsorption isotherms which indicates the presence of attractive forces between molecules. Thus, both the inductive and conjugative effects lead to a reduction in repulsive forces between adjacent adsorbed molecules. The inhibition may thus be attributed to the above effects being more dominant than steric hindrance.

Inhibition of metal dissolution in aqueous media involves adsorption of the organic molecule at the metal interface. This may be either physisorption in which case electrostatic forces are involved or chemisorption which involves charge transfer or charge sharing [12]. Electron transfer in chemisorption can occur in molecules having loosely bound electrons or in molecules having π electrons. It has been shown that ΔG^o_{ads} values less than $-42.0\,kJ\,mol^{-1}$ are typical of charge sharing [12]. The results reported here give a ΔG^o_{ads} value of $-46.3\,kJ\,mol^{-1}$. BHDC was adsorbed both via the positively charged nitrogen atom and the electrons of the benzene ring. Similar modes of adsorption have been shown in phosphorus-containing compounds [13]. These workers report that adsorption via the π electrons predominates over adsorption via the positively charged cation. This is also the case in the present study as the anodic dissolution reaction was inhibited by the organic molecule.

4. Conclusions

(i) BHDC is an anodic inhibitor of carbon dioxide corrosion of iron but is not very effective at moderately high temperatures around 60° C.

(ii) The mechanism of corrosion involves charge transfer control both in the presence and absence of the inhibitor.

(iii) The Frumkin isotherm describes the experimental findings presented in this paper. The inhibitor molecule displaces five water molecules at the surface.

(iv) The standard free energy of the adsorption, ΔG^o_{ads}, was found to be $-46.3\,kJ\,mol^{-1}$ at 30° C indicating the spontaneity of the process.

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