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Adsorption and corrosion inhibition properties of thymol

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On the basis of electrocapillary and differential capacitance measurements it was established that thymol from acid solutions was adsorbed on a mercury electrode. The shape of the thymol adsorption isotherm, the positive value of the attraction constant a and the position of the minimum of the $\partial \ln c/\partial\theta$ vs θ dependence (where c is thymol concentration and θ is electrode coverage) indicated the applicability of the Frumkin equation.

The characteristics of thymol as a corrosion inhibitor were studied by observing the dissolution of aluminium and zinc in hydrochloric acid with and without thymol addition. The values of the reaction numbers (*RN*) plotted against thymol concentration were compared with the adsorption curves. The analysis of the results, i.e. the comparison of the $RN(c)$ and $\theta(c)$ curves for the liquid and solid metal electrodes and the difference between the $RN(c)$ curves for aluminium and zinc, indicated a different adsorption mechanism and also a different corrosion inhibition efficiency by thymol for aluminium and zinc.

1. Introduction

It is known that surface active substances adsorbed on a metal change the metal–electrolyte interface and affect the rates of corrosion processes. Since they are adsorbed all over the metal surface they are, as a rule, double acting inhibitors and retard both anode and cathode processes. For the estimation of the inhibition efficiency of surfactants numerous methods are available [1]. In the present work the thermometric corrosion test was used and the results were compared with adsorption data derived from electrocapillary and differential capacitance measurements.

The aim of our investigations was directed toward examining the possibility of obtaining data on the characteristics of thymol as a corrosion inhibitor by a simple and cheap thermometric test which can therefore find application in industrial corrosion inhibition research.

2. Experimental details

Electrocapillary measurements [2] performed using a Lippman capillary electrometer and an impedance bridge [3] constructed in this laboratory provided the data for the dependences of differential capacitance on potential for a Hg electrode in a solution containing 0.1 mol dm^{-3} $HClO_4$ with various additions of thymol. Calibration of the above systems was performed by comparing the results of our measurements for the Hg electrode in LiCl with data from the literature [4, 5]. Potentials were referred to the saturated calomel electrode and temperature was maintained at 25 ± 0.2° C. Commercially available samples of aluminium and zinc were used and temperature–time curves during dissolution of the metals in 2 mol dm^{-3} HCl with and without thymol additions were obtained. The reaction vessel was of the form described in [6].

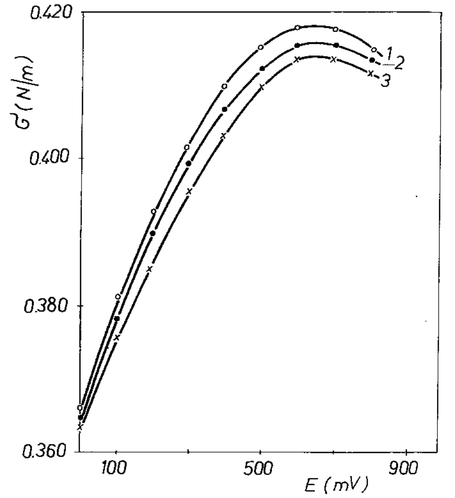

Fig. 1. Electrocapillary curves (surface tension σ vs potential E) in $2\,\mathrm{mol\,dm^{-3}}$ $HClO_4$ with thymol additions. $c(\mathrm{mol\,dm^{-3}})$: (1) 0; (2) 7.5×10^{-4}; (3) 2.5×10^{-3}.

3. Results

Fig. 1 shows the electrocapillary curves for the Hg electrode in $2\,\mathrm{mol\,dm^{-3}}$ $HClO_4$ when different amounts of thymol are added. The differential capacitance curves for the Hg hanging drop electrode in $0.1\,\mathrm{mol\,dm^{-3}}$ $HClO_4$ acting as a supporting electrolyte with different thymol additions at a frequency of 10^3 Hz are presented in Fig. 2. The dependence of the reaction temperature on time for the dissolution of aluminium and zinc in $2\,\mathrm{mol\,dm^{-3}}$ HCl containing thymol can be seen from Figs 3 and 4 respectively.

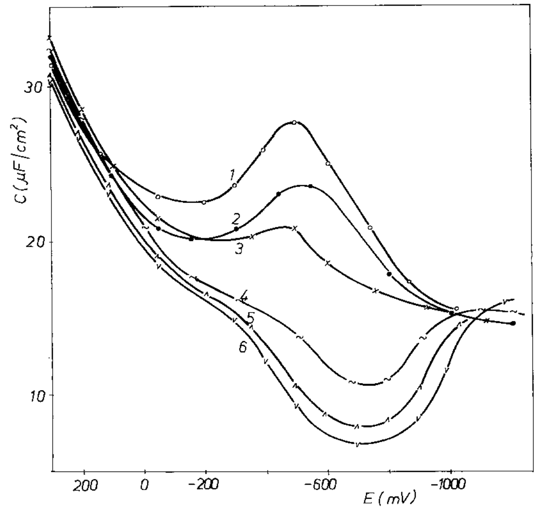

Fig. 2. Differential capacitance curves for Hg electrode in $0.1\,\mathrm{mol\,dm^{-3}}$ $HClO_4$ with various thymol additions. $c(\mathrm{mol\,dm^{-3}})$: (1) 0; (2) 1×10^{-5}; (3) 2.5×10^{-5}; (4) 1×10^{-4}; (5) 2.5×10^{-4}; (6) 5×10^{-4}.

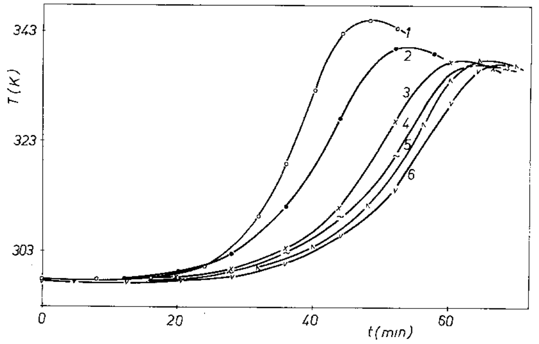

Fig. 3. Reaction temperature (T) as a function of time (t) for aluminium in $2\,\mathrm{mol\,dm^{-3}}$ HCl with various thymol additions. $c(\mathrm{mol\,dm^{-3}})$: (1) 0; (2) 7.5×10^{-5}; (3) 1×10^{-4}; (4) 2.5×10^{-4}; (5) 5×10^{-4}; (6) 1×10^{-3}.

4. Discussion

The electrocapillary maxima (Fig. 1) for the Hg electrode in acid solution containing thymol are lowered. The position of the minima of the $C(E)$ curves (where C is differential capacitance and E is potential) at constant frequency (Fig. 2) depends on thymol concentration indicating that organic molecules are adsorbed on the Hg electrode. The explanation of the shape of the $C(E)$ curves according to [7, 8] is as follows. At low thymol concentration (curves 2 and 3) and also at positive electrode charge (the beginning

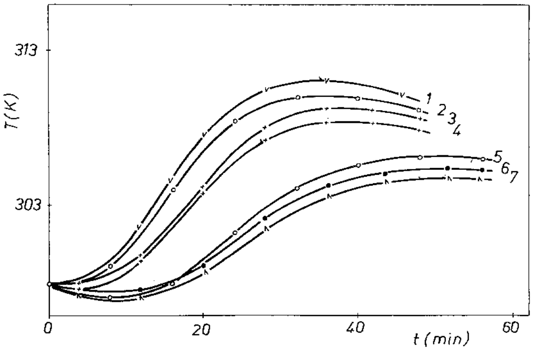

Fig. 4. Variation of reaction temperature (T) with time (t) for zinc in $2\,\mathrm{mol\,dm^{-3}}$ HCl with various thymol additions. $c(\mathrm{mol\,dm^{-3}})$: (1) 0; (2) 1×10^{-5}; (3) 5×10^{-5}; (4) 5×10^{-4}; (5) 7.5×10^{-4}; (6) 1×10^{-3}; (7) 2×10^{-3}.

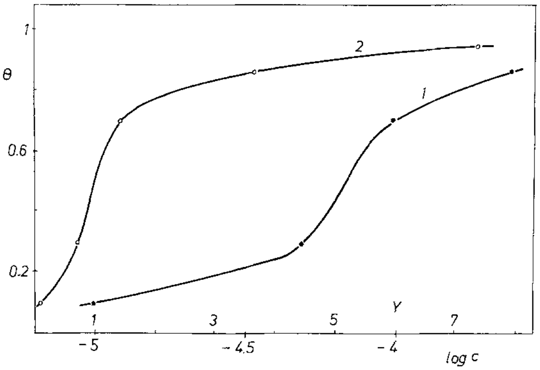

Fig. 5. Dependence of electrode coverage θ by thymol molecules at $-700\,\text{mV}$ on (1) log c; (2) y.

of the $C(E)$ curve) the interaction with the electrons of the aromatic nuclei results in their flat orientation. At higher thymol concentrations in the potential range 100–300 mV a repulsive interaction between thymol molecules occurs. On the other hand if the negative potential is increased a perpendicular reorientation of the adsorbed molecules occurs and a consequent marked decrease of capacity results. That this happens can be seen from Fig. 2 (curves 4, 5, 6). The electrode coverage reaches maximum at ≈ -700 mV.

The electrode coverage θ is calculated using the relation

$$\theta = \frac{C_0 - C}{C_0 - C'} \tag{1}$$

from [9], where C, C_0 and C' are capacities for θ, $\theta = 0$ and $\theta = \theta_{\max}$, respectively. Fig. 5 shows the dependence of θ on the logarithm of concentration and on the relative concentration $y = c/c_{\theta=0.5}$ at $-700\,\text{mV}$. From the experimental data and the Frumkin isotherm taken from [8] and written in the form

$$y = \frac{c}{c_{\theta=0.5}} = \frac{\theta}{1-\theta}\exp\left[a(1 - 2a\theta)\right] \tag{2}$$

the attraction constant a is determined. Positive values are obtained from Equation 2 and also from the slope of the $\theta(y)$ curve at $\theta = 0.5$, being 0.94 and 1.25 respectively. According to [10] at constant E and for a Frumkin isotherm the minimum of the dependence of $\partial \ln c/\partial\theta$ on θ lies at $\theta = 0.5$. The curve in our measurements exhibits a minimum at $\theta = 0.55$ (Fig. 6). This satisfactory agreement between the experimental and theoretical values, the positive sign of the constant a and also the sigmoidal shape of the adsorption isotherm confirm the applicability of the Frumkin equation for the description of the adsorption process of thymol from acid solution on the Hg electrode.

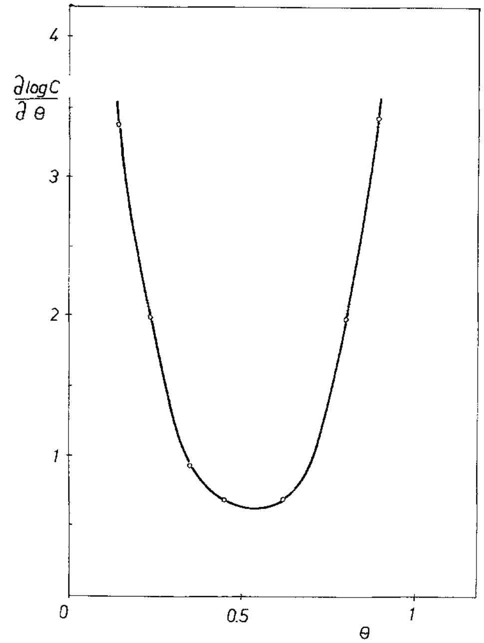

Fig. 6. Dependence $\partial \log c/\partial\theta$ on electrode coverage θ at -700 mV.

Earlier Aziz and Shams El Din [6] observed a decrease in the dissolution rate of aluminium and zinc in the presence of organic species in HCl and this behaviour was explained taking into account the adsorption of the organic molecules acting as inhibitors on the metal surface and their competition with agressive Cl^- ions. In spite of the fact that thymol is adsorbed on the Hg electrode it does not mean that it can act as a corrosion inhibitor for metal solid electrodes. The possibility of corrosion inhibition was tested by examining the reaction temperature during the dissolution of zinc and aluminium.

The parameters T_m and T_i from the curves representing temperature–time dependence (Figs 3, 4) define the reaction number RN,

$$RN = (T_m - T_i)/t \tag{3}$$

where T_i is the initial and T_m the maximum temperature; in time t (min) the temperature T_m

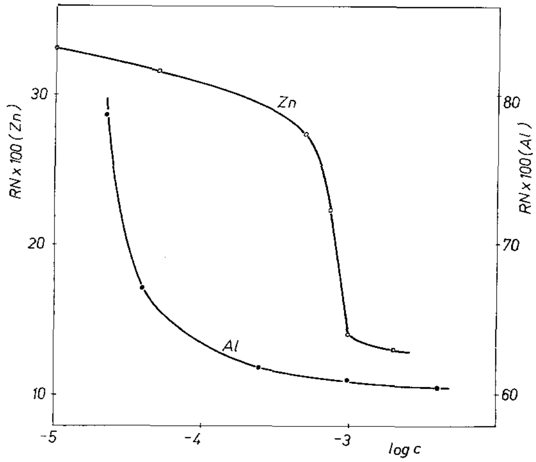

Fig. 7. Reaction number (*RN*) as a function of logarithm of thymol concentration (c) in 2 mol dm^{-3} HCl.

is reached. In Fig. 7 the RN values for aluminium and zinc are plotted as a function of the logarithm of the thymol concentration. According to Aziz and Shams El Din [6] these curves may be treated as adsorption curves of thymol from acid solutions. For aluminium the curve has a shape approximately the inverse of a logarithmic dependence while for zinc it is sigmoidal in shape. According to Frumkin the former dependence indicates a repulsive interaction and the latter an attractive interaction between the organic molecules [11].

Thus there is no doubt that adsorption of thymol on liquid as well as on solid electrodes occurs but the adsorption mechanisms are not the same. The attraction between organic molecules increases the thymol inhibition efficiency and therefore thymol is a better inhibitor for zinc than for aluminium. The characteristics of thymol as a superior corrosion inhibitor for zinc than for aluminium were tested in a preliminary manner in this laboratory through weight loss measurements.

In concluding it seems that the thermometric method is more useful for the estimation of inhibition efficiency of organic substances than measurements of the double layer parameters because of the difficulties of dealing with solid metals [12]. At the same time doubtful conclusions could be drawn if results from measurements on liquid electrodes were applied to solid ones.

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