Adsorption of *N*-phenylmaleimide and its derivatives on iron electrodes in sulfuric acid solutions

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The adsorption of *N*-(phenyl)maleimide and its derivatives on iron electrodes in sulfuric acid medium has been studied by the capacitance method. The process investigated is well described by Frumkin's isotherm. The adsorption parameters characterizing the interaction forces between the species in the adsorbed layer, the area occupied by each species and the maximum surface excess have been calculated on the basis of this isotherm. Combining data from the electrochemical method with quantum-chemical calculations of the chemical structure and the partial electronic charges of the compounds studied a mechanism of adsorption on the iron surface is proposed. The inhibiting effect observed is explained in relation to the adsorption behaviour.

1. Introduction

The inhibiting action of organic compounds with respect to metal corrosion in aggressive media is most often related to their adsorption on the metal surface [1-8]. The latter process results in an effective blocking of the active sites of metal dissolution and/or hydrogen evolution, which results in a considerable decrease in the overall corrosion rate.

N-(phenyl)maleimide and its methyl and bromo-containing derivatives are of interest as inhibitors of iron corrosion because there are active centres in their molecules which favour the adsorption of the molecules on the iron surface. It was found, in previous investigations [9-11] related to the inhibiting and adsorptive behaviour of maleimide and its *p*-phenyl substituted derivatives on iron in acid and neutral media, that some of these compounds exhibited good adsorption in acid medium.

To elucidate the mechanism of the adsorption and the inhibiting action, it is necessary to obtain information on the main adsorption characteristics, that is, the degree of metal surface coverage with surfactant species, the adsorption equilibrium constant, the maximum surface excess of the adsorbed substance and the attraction constant. The inhibiting properties and the adsorption behaviour of several indenone derivatives on polycrystalline iron were investigated mainly using capacitance measurements. The results obtained were reported in a recent series of papers [12-14].

The present work is concerned with the study of the adsorptive and inhibiting behaviour of *N*-(phenyl)-maleimide and its methyl and bromo-containing derivatives on iron in acid medium. The data obtained are discussed taking into consideration the results from the quantum-chemical calculations of the structure and the partial electron charge distribution in the substances molecules.

2. Experimental details

The present study uses the capacitance method in 0.1 M H_2SO_4 as a model corrosion medium. A cylindrical electrode made of spectral purity grade Fe (15 ppm) was used. The electrode was polished both mechanically and chemically to obtain a reproducible surface area. It was thoroughly washed with doubly distilled water and subjected to cathodic polarization for an hour in 0.015 M H_2SO_4 under continuous hydrogen bubbling and again thoroughly washed with doubly distilled water. The electrode, already under current, was then immersed in the cell. The solution was saturated with hydrogen prior to the experiment. This procedure resulted in a mean roughness factor of 1.66, determined by a well known procedure [15]. The capacitance was evaluated with respect to the real electrode surface area.

The measurements were carried out in a conventional three-electrode cell. The counter electrode consisted of a Pt mesh positioned symmetrically around the working electrode. A saturated calomel electrode was used as reference. All potential values cited are referred to the NHE.
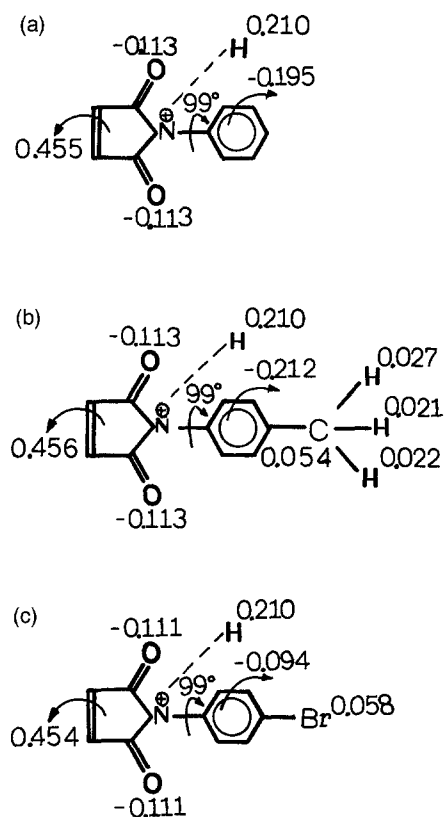
Fig. 1. Molecular structure and distribution of partial charges in the protonized molecules of: (a) N-(phenyl)maleimide; (b) N-(p-tolyl)-maleimide; (c) N-(p-bromophenyl)maleimide.

The solutions were prepared from analytical grade H_2SO_4 (Merck) and doubly-distilled water. The organic inhibitors studied were synthesized in house. Their purity was controlled by TLC and infrared spectroscopy. The inhibitor was introduced to the working medium in the form of an ethanol solution. The concentration of the latter was 2 vol %, while that of the organic substance varied in the range $0.05–5\,\mu\mathrm{mol}\,\mathrm{dm}^{-3}$.

Purified hydrogen was bubbled through the solution during the experiments.

The differential capacitance of the iron electrode was recorded using AC P-568 bridge at a frequency of 870 Hz. Preliminary investigations [12, 14] showed that the differential capacitance of the iron electrode was practically independent of the perturbation frequency for frequencies above 800 Hz.

Quantum-chemical calculations were carried out with the application of MNDO method [16]. They were aimed at determination of the partial electron charges of the atoms in the molecules as well as of the bond lengths, of the valency and dihedral angles. The data obtained provided information on the partial charges in the five-atom imide ring and in the benzene residue. The geometric area of the different radicals and groups, as well as of the entire molecules, were also determined. For calculation of the geometric area of N-(phenyl)maleimide, N-(p-tolyl)maleimide and N-(p-bromophenyl)maleimide, it was taken into account that the benzyl residue is positioned in a preferred conformational state, perpendicular to the plane of the five-atom imide ring (Fig. 1).

It is also known that maleimide and its derivatives protonize in acid medium at the nitrogen atom of the five-atom ring where bonding with H^+ from the solution takes place (this is the preferred state).

3. Results

The differential capacitance against potential relationships for the iron electrode in aqueous ethanol solutions of 0.1 M H_2SO_4 with and without the addition of N-(phenyl)maleimide, N-(p-tolyl)maleimide and N-(p-bromophenyl)maleimide are plotted in Fig. 2(a), (b) and (c), respectively.

The effect of the ethanol additive can be seen by comparing curves 1 and 1′ (Fig. 2). This effect is negligible and is exerted mainly in the cathodic branch of the curve.

The addition of N-(phenyl)maleimide and its methyl and bromo-derivatives to the blank solution affects the character of the C/E-curves, as well as the values of the iron electrode capacitance. The latter decreases with increase in the organic additive concentration. It varies with the substance introduced due to its dependence on the different adsorbability on the electrode surface. The greatest decrease is observed in the presence of N-(p-bromophenyl)maleimide. It is seen from Fig. 2(a), (b) and (c) that the adsorbability order is N-(p-bromophenyl)maleimide > N-(p-tolyl)maleimide > N-(phenyl)maleimide.

The C/E relationships presented in Fig. 2(a), (b) and (c) show that the adsorption process shifts the capacitance minimum to more negative potentials. It is important to emphasize that the region of minimum capacitance values is outside the corrosion potential range. This explains why the inhibiting effect is not very high, especially in the cases of strong adsorbability under conditions of iron self dissolution (i.e., at free corrosion potential).

Quantitative evaluation of the adsorbability of organic substances on the iron/H_2SO_4 solution interface can be obtained from the adsorption isotherms which give the correlation between surface and bulk concentrations of the organic substances. The degree of metal electrode surface coverage (θ) is calculated using the experimental values of the capacitance by the application of the well known formula [17]:

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

where C_0 is the capacitance minimum for iron in the blank solution and C is the capacitance minimum for a definite bulk concentration of the surfactant; C' is the capacitance for $\theta = 1$. C' was estimated from the cross point of the anodic and the cathodic linear branches of the $1/C$ against $1/E$ relationship for the maximum additive concentration.

The degree of coverage against concentration for the compounds studied are shown in Fig. 3. It can be concluded that: (i) the degree of surface coverage by the bromo-derivative is greater (curve 3) than that by the other compounds; and (ii) the maximum
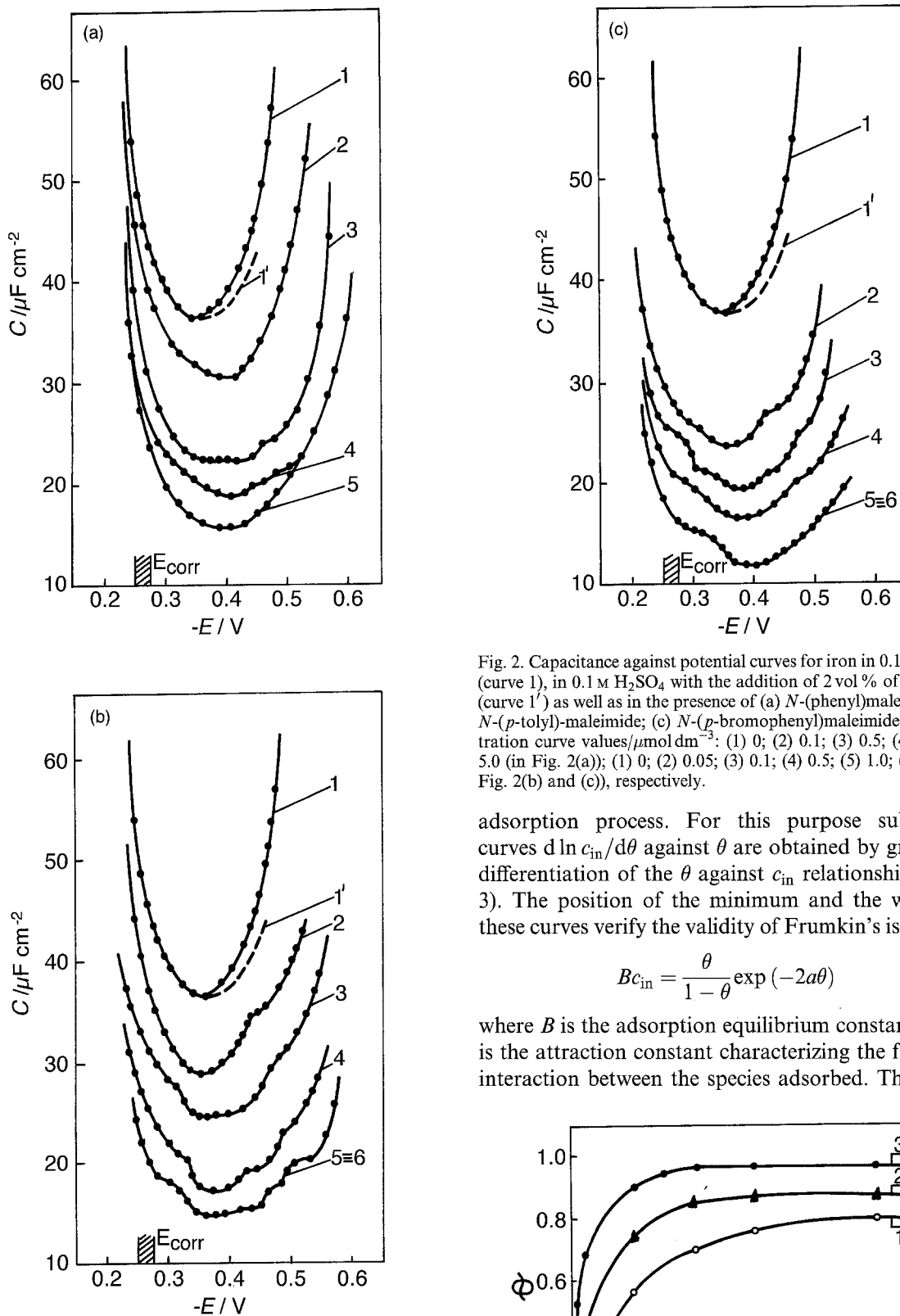
Fig. 2. Capacitance against potential curves for iron in 0.1 M H_2SO_4 (curve 1), in 0.1 M H_2SO_4 with the addition of 2 vol % of C_2H_5OH (curve 1') as well as in the presence of (a) N-(phenyl)maleimide: (b) N-(p-tolyl)-maleimide; (c) N-(p-bromophenyl)maleimide. Concentration curve values/μmol dm^{-3}: (1) 0; (2) 0.1; (3) 0.5; (4) 1.0; (5) 5.0 (in Fig. 2(a)); (1) 0; (2) 0.05; (3) 0.1; (4) 0.5; (5) 1.0; (6) 5.0 (in Fig. 2(b) and (c)), respectively.

adsorption process. For this purpose subsidiary curves $d \ln c_{in}/d\theta$ against θ are obtained by graphical differentiation of the θ against c_{in} relationships (Fig. 3). The position of the minimum and the width of these curves verify the validity of Frumkin's isotherm:

$$Bc_{in} = \frac{\theta}{1-\theta} \exp\left(-2a\theta\right) \qquad (2)$$

where B is the adsorption equilibrium constant and a is the attraction constant characterizing the forces of interaction between the species adsorbed. The linear

value of θ ($\theta_{max} = 0.97$) is reached in the latter case at an essentially low concentration ($c_{in} = 1\ \mu$mol dm^{-3}). The comparative consideration shows that θ_{max} reaches a value of 0.87 in the presence of N-(p-tolyl)-maleimide at $c_{in} = 1.5\ \mu$mol dm^{-3} and a value of 0.80 in the presence of N-(phenyl)maleimide at $c_{in} = 2.5\ \mu$mol dm^{-3}.

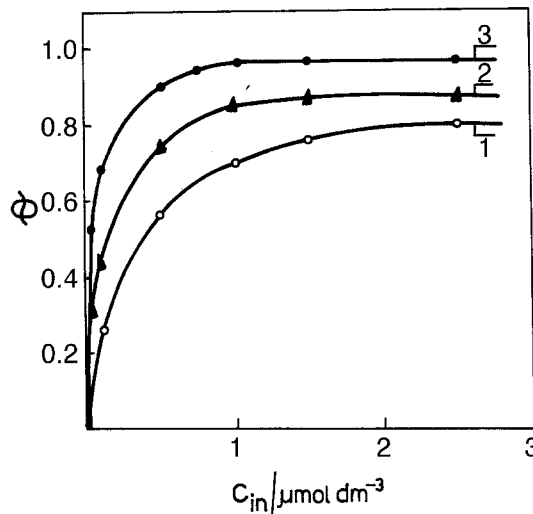A criterion offered by Damaskin [18] is used to determine the validity of the isotherm describing the

Fig. 3. Surface coverage against additive concentration for (1) N-(phenyl)maleimide; (2) N-(p-tolyl)maleimide and (3) N-(p-bromophenyl)maleimide.
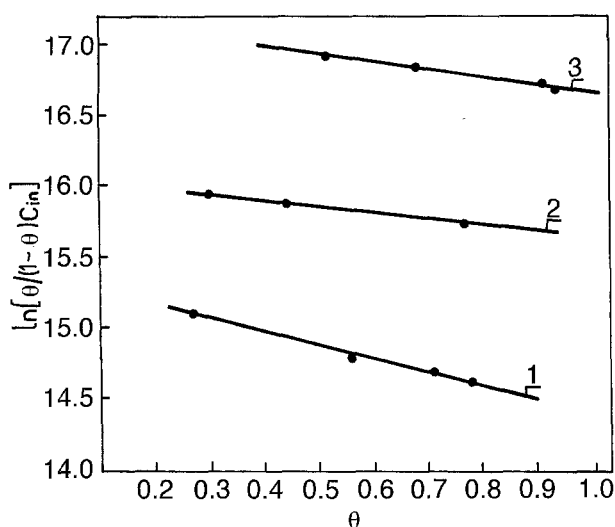
Fig. 4. Dependence of $\ln[\theta/(1-\theta)c_{in}]$ on θ in correspondence with Frumkin's isotherm describing adsorption in 0.1 M H_2SO_4 of (1) N-(phenyl) maleimide; (2) N-(p-tolyl)maleimide and (3) N-(p-bromophenyl)maleimide.

character of the dependence in the coordinates in $[\theta/(1-\theta)c_{in}]$ against θ (Fig. 4) confirms the validity of Frumkin's isotherm.

A more accurate determination of the attraction constant a is achieved using an algorithm offered by Damaskin [19]. The latter requires the introduction of relative concentration values, i.e. $y = c/c_{\theta=0.5}$. The value of $c_{\theta=0.5}$ is obtained from the plot of θ against c_{in} (Fig. 3). The attraction constant from Frumkin's isotherm is calculated by the application of Equation 3:

$$a = \frac{1}{1-2\theta}\ln\left[\frac{y(1-\theta)}{\theta}\right]$$ (3)

while the equilibrium constant B is estimated from the following ratio:

$$B = \frac{\exp(-a)}{c_{\theta=0.5}}$$ (4)

The method of iteration has been used in this case.

The calculated values of a and B are summarized in Table 1. The values of the free energy of adsorption $(-\Delta G_A)$ are also presented. These are calculated using Equation 5:

$$B = \frac{1}{55.5}\exp\left(\frac{-\Delta G_A}{RT}\right)$$ (5)

The negative values of the attraction constant are an indication of the presence of repulsive forces between the species in the adsorbed layer. The com-

parison of the values of B and of $(-\Delta G_A)$ characterizing the adsorption process of N-(phenyl)maleimide and its methyl and bromo-derivatives on the iron electrode in sulfuric acid medium verifies the conclusion concerning the adsorbability of the compounds studied. The value of B obtained in the presence of N-(p-bromophenyl)maleimide is from 3 to 6 times greater than that obtained in the presence of N-(p-tolyl)maleimide and N-(phenyl)maleimide.

If the adsorption process is realized so that the electrode charge is a function of the potential and of the degree of surface coverage, that is, $q = q(E,\theta)$ and the adsorption equilibrium is established for each potential value, then Frumkin's adsorption isotherm can be applied for the determination of the surface excess (Γ_m). The dependence of the adsorption equilibrium constant on the potential may be presented in the form [20]:

$$B = B_{max}\exp\left[-b(E - E_m)^2\right]$$ (6)

where $B_{max} = B$ at $E = E_m$; E_m is the potential of maximum adsorption, while b is the slope of the linear dependence of $\{\ln[\theta/(1-\theta)] - 2a\theta\}$ against $(E - E_m)^2$, that is,

$$b = \frac{(C_0 - C') \times 10^{-6}}{RT\Gamma_m}$$ (7)

Hence, Γ_m is obtained from

$$\Gamma_m = \frac{(C_0 - C') \times 10^{-6}}{RTb}$$ (7')

The area occupied by each adsorbed molecule is obtained from the ratio

$$S = \frac{1}{\Gamma_m N_A}$$ (8)

The analysis of the C/E-relationships obtained at the maximum concentration of the additive leads to a linear relationship between $\{\ln[\theta/(1-\theta)] - 2a\theta\}$ and $(E - E_m)^2$. The latter are presented in Fig. 5(a) for N-(phenyl)maleimide, in Fig. 5(b) for N-(p-tolyl)-maleimide (lines 1 and 1') and for N-(p-bromophenyl)-maleimide (lines 2 and 2'), respectively.

It can be concluded from Fig. 5 that: (i) the adsorption of N-(phenyl)maleimide is characterized by one adsorption state for $E < E_m$ (line 1) and by another for $E > E_m$ (line 1'); (ii) the adsorption of N-(p-tolyl)-maleimide and N-(p-bromophenyl)maleimide (Fig. 5(b)) is characterized by two adsorption states for potentials $E < E_m$. The first one (lines 1 and 2) corresponds to a vertical orientation while the second

Table 1. Summary of parameters characterizing the adsorption of N-(phenyl)maleimide and its derivatives on the iron electrode in 0.1 M H_2SO_4

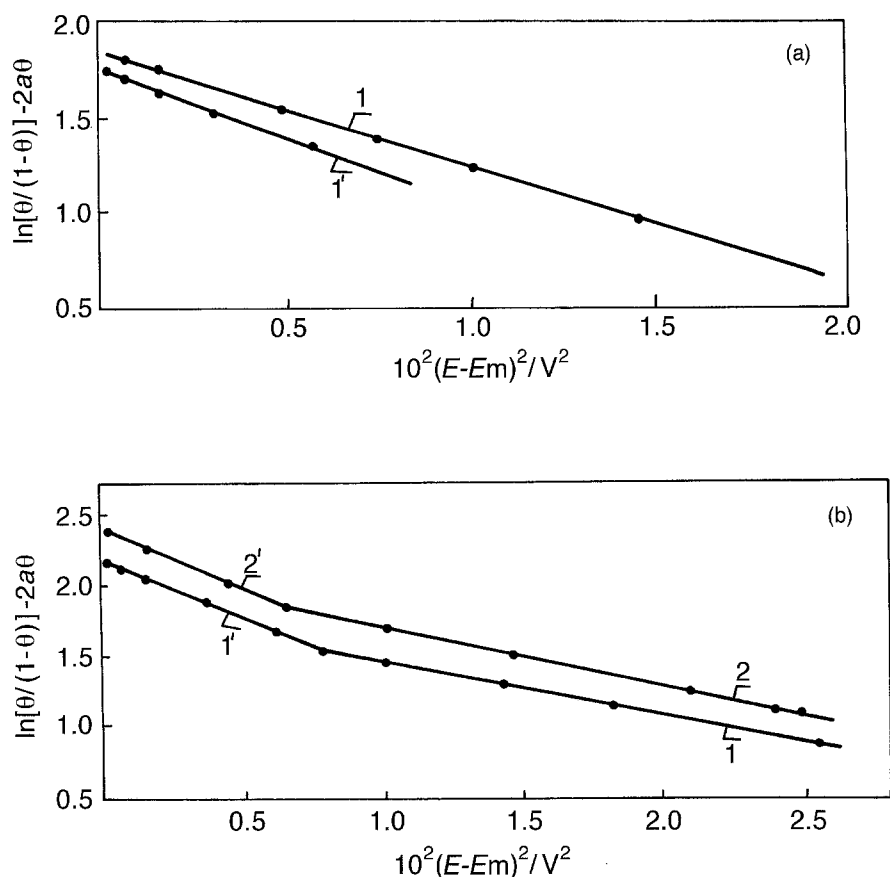| Substance	a	$10^{-6}B$	$(-\Delta G_A)$ /kJ mol^{-1}	I state		II state	
				$10^{10}\Gamma_m$ /mol cm^{-2}	S_1 /(nm)^2	$10^{10}\Gamma_m$ /mol cm^{-2}	S_2 /(nm)^2
N-(phenyl)maleimide	−0.37	3.9	46.7	2.91	0.57	2.54	0.65
N-(p-tolyl)maleimide	−0.16	8.6	48.6	4.30	0.39	2.16	0.77
N-(p-bromophenyl)malemide	−0.25	25.6	51.3	4.26	0.39	2.29	0.73

Fig. 5. (a) Dependence of $\{\ln[\theta/(1-\theta)] - 2a\theta\}$ on $(E - E_m)^2$ obtained in 0.1 M H_2SO_4 solution of N-(phenyl)maleimide. (b) N-(p-tolyl)maleimide (curves 1 and 1') and N-(p-bromophenyl)maleimide (curves 2 and 2').

state (lines 1' and 2') to a horizontal orientation resulting from π-electron interaction of the phenyl radical with the electrode surface.

4. Discussion

An explanation of the difference in the adsorption behaviour of the compounds studied is attempted on the basis of the values of the adsorption parameters obtained and the data provided by the quantum chemical calculations. Moreover, a hypothesis concerning the possible orientation of the molecules adsorbed can be advanced.

The data on the structure and the distribution of the partial electron charges in the protonized forms of N-(phenyl)maleimide, N-(p-tolyl)maleimide and N-(p-bromophenyl)maleimide (Fig. 1) suggest the following:

(i) that the phenyl radical is disposed perpendicularly to the plane of the five atom imide ring;

(ii) that the partial positive charge localized in the five atom imide ring and the partial negative charge at the oxygen atom of the carbonyl group in the molecule of N-(phenyl)maleimide and in the molecules of its derivatives change insignificantly;

(iii) that additional partial positive charge is observed in the molecules of N-(p-tolyl)maleimide and of N-(p-bromophenyl)maleimide. This is localized at the atoms of the corresponding substituents which leads, in turn, to a variation in the partial negative charge of the benzene residue.

As has already been mentioned, the adsorption of

N-(phenyl)maleimide is characterized by two adsorption states, the first at $E < E_m$, and the second at $E > E_m$. The values of the areas of the adsorbed species in both adsorption states are 0.57 and 0.65 (nm)^2, respectively. Hence, it can be assumed that the molecule of N-(phenyl)maleimide is adsorbed horizontally in both potential ranges. The quantum chemical calculations show, as already pointed out, that the five-atom ring and the benzene residue are positioned at an angle of 99°. Thus it is reasonable to accept that the horizontal adsorption of N-(phenyl)maleimide occurs in the cathodic region (at $E < E_m$) through the imide ring, where a partial positive charge is localized. In this case the phenyl radical is positioned perpendicularly to the plane of the five-atom ring (i.e., the adsorption plane). The phenyl radical is adsorbed horizontally, at the expense of π-electron interaction, in the anodic region (at $E > E_m$), while the imide ring is positioned perpendicularly to the adsorption plane. The preorientation of the molecule of N-(phenyl)-maleimide on the electrode surface proceeds with large conformational freedom, because the bond between the nitrogen and the carbon atom in the phenyl radical is simple. In the second state, where the imide ring is oriented perpendicularly to the electrode surface, the adsorption of one of the oxygen atoms also results from π-electron interaction, while the other oxygen atom is positioned in the outer adsorption layer.

It follows from Fig. 5(b) that the preorientation of the adsorbed molecules of N-(p-tolyl)maleimide (lines 1 and 1') and of N-(p-bromophenyl)maleimide (lines 2 and 2') proceeds in the cathodic potential range $(E < E_m)$. The values of the areas occupied by the

molecule of N-(p-tolyl)maleimide in both adsorption states are 0.39 and 0.71 $(nm)^2$, while those of the molecule of N-(p-bromophenyl)maleimide are 0.39 and 0.73 $(nm)^2$, correspondingly. These data suggest that the first adsorption state, where the areas of both organic molecules are the same, corresponds to a vertical, and the second one to a horizontal, orientation. The vertical orientation of the molecules of N-(p-tolyl)maleimide and of N-(p-bromophenyl)-maleimide is possible at $E < E_m$ because of the presence of partial positive charges at the methyl group and at the bromine atom. The horizontal adsorption results from π-electron interaction of the benzene residue and of one of the oxygen atoms (that from the carbonyl group) with the electrode surface. It follows from the quantum-chemical calculations (Fig. 1) that the π-electron interaction is the greatest in the case of N-(p-tolyl)maleimide adsorption as a result of the larger electron density of the benzene residue.

The areas calculated in the case of horizontal orientation of the molecules (Table 1, state 2) resulting from π-electron interaction are very close to the quantum chemical data on the geometric areas, which are in fact 0.62 $(nm)^2$ for N-(phenyl)maleimide, 0.75 $(nm)^2$ for N-(p-tolyl)maleimide and 0.73 $(nm)^2$ for N-(p-bromophenyl)maleimide.

The comparison of the electrochemical data and the values of the adsorption parameters (B and $-\Delta G_A$) leads to the conclusion that N-(p-bromophenyl)-maleimide exhibits the greatest adsorbability. This fact may be explained by the peculiarities of the $+M$ of the bromine atom which increases under dynamic conditions (i.e., in the course of the adsorption process) leading to variation in the electron density of the benzene residue.

5. Conclusions

This study, using the capacitance method of the adsorption and of the inhibiting behaviour of N-(phenyl)maleimide, N-(p-tolyl)maleimide and N-(p-bromophenyl)maleimide on iron in acidic medium, suggests the following:

(i) The adsorbability order is N-(p-bromophenyl)-maleimide > N-(p-tolyl)maleimide > N-(phenyl)-maleimide.

(ii) The adsorption of the substances investigated is described by Frumkin's isotherm.

(iii) Preorientation of the molecules of the three substances is found. This depends on the potential of the iron electrode. A hypothesis for the possible orientation of the molecules is advanced on the basis of data regarding their structure and partial charges.

(iv) It is found that N-(phenyl)maleimide and its methyl and bromo-containing derivatives exhibit a medium inhibiting effect.

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