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Synergism in copper corrosion inhibition by sodium dodecylbenzenesulphonate and 2-mercaptobenzoimidazole

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Abstract The inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and 2-mercaptobenzoimidazole (2-MBI) on the corrosion of copper in sulphuric acid solution have been studied using electrochemical impedance spectroscopy (EIS) and Tafel polarisation measurements. For 2-MBI, a monotonic increase in inhibition efficiency is observed as a function of concentration. Upon mixing 2-MBI and SDBS, concentration regions showing synergistic inhibition behaviour are identified and it is concluded that electrostatic interactions between adsorbate ions are likely responsible for both phenomena. Different adsorption isotherms were tested for relevance in describing the adsorption behaviour of both 2-MBI and SDBS. 2-MBI obeys the Langmuir isotherm and SDBS adsorption is described successfully by the Temkin isotherm.

Keywords Inhibitors · Sodium

dodecylbenzenesulphonate · 2-Mercaptobenzoimidazole · Copper · Pickling · Synergistic effect

1 Introduction

Acid solutions are extensively used in various fields of industry: in pickling operations in order to remove scales from the surface of metals and in cleaning heat exchanging

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H. Tavakoli · T. Shahrabi Department of Materials Science, Faculty of Engineering, Tarbiat Modarres University, Tehran, Iran apparatus to remove deposits. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media [1-10]. Inhibitors are commonly used in those processes to control the metal dissolution as well as acid consumption. Within the group of nitrogen containing inhibitors, amines have received considerable attention, as their protonation in acidic media yields cationic species that show good inhibitive performance for steel. Hexamethylenetetramine (HA, C₆H₁₂N₄, also called hexamine or urotropine) is probably the most widely studied amine for this purpose. In order to further improve the performance of HA as inhibitor of acid corrosion, identifying synergistic effects with other additives has been the subject of several investigations. Usually, combining HA (more precisely HAH_n^{+n} with n = 1-4 in acid solution) with an anionic species yields the required enhancement through electrostatic interactions between oppositely charged ions. For hexamethylenetetramine (HA) in fairly concentrated (3 mol dm⁻³) hydrochloric acid solutions, synergistic effects can be achieved by addition of certain metal cations such as Cu²⁺, As³⁺, Sb³⁺ and Sn²⁺ [8]. The improved performance of HA in these cases is believed to rely on the formation of anionic complexes such as $CuCl_4^{2-}$ or AsO_2^{-} in the strongly acidic solution. Irrespective of the synergistic effects that may obtained through this approach, the use of heavy metal ions for this purpose seems rather questionable, especially in large-scale industrial applications such as acid pickling. An approach that is less worrisome from an environmental point of view involves the use of ionic surfactants as co-inhibitors. The study of surfactants adsorbed on metal surfaces is extremely important in a variety of fields such as corrosion inhibition and metal electrodeposition. In a previous paper [1], the inhibition effects of sodium dodecylbenzenesulphonate (SDBS) on the corrosion of mild steel in

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sulphuric acid solution was reported. It was shown that SDBS acts as a corrosion inhibitor and presents a synergistic effect on the inhibitive action of HA. Recently, Villamil et al. [9] observed a synergistic effect of sodium dodecylsulphonate SDS and Benzotriazole (BTAH) on the corrosion inhibition of stainless steel (304 SS) in 2.0 mol dm⁻³ sulphuric acid at several BTAH-SDS concentration ratios. SDS has a corrosion inhibitive effect for iron [8] and aluminum in sodium chloride media [11]. 2-MBI as inhibitor has been studied for mild steel in sulphuric [12] and phosphoric [13] acid solutions and for brass (60/40) in ammonia solution [14].

We have studied the mechanism of adsorption of 2-MBI on Au(111) and Cu(111) [15–17]. Our previous study of adsorption of 2-MBI on Cu(111) by electrochemical impedance spectroscopy (EIS), polarization modulation and infrared reflection adsorption spectroscopy has shown that 2-MBI is one of the best corrosion inhibitors for copper [17].

In the present paper, the effects of combining 2-MBI with the anionic surfactant SDBS on copper corrosion inhibition in 0.5 mol dm⁻³ H₂SO₄ are discussed. Corrosion rates were determined from Tafel linear extrapolation and electrochemical impedance spectroscopy and results interpreted in terms of what likely occurs on a microscopic scale at the metal/electrolyte interface. Several isotherms are tested for their potential relevance in describing the adsorption behavior of the studied compounds and the interaction between the inhibitors upon mixing is analyzed by calculating synergism parameter values.

2 Experimental

2.1 Materials

For polarization and EIS measurements, copper specimens with composition (in wt.%) Al 0.003, Fe 0.02, Pb 0.02, Sn 0.004, Zn 0.014, Mg 0.02, P 0.001, Mn 0.001, S 0.002, Sb 0.05, Cu (balance) with the 1 cm² of electrode surface area were used. The samples were polished to a mirror finish using emery paper followed by aqueous alumina suspensions with particle sizes 0.05–0.1 μ m, decreased by sonication in analytical reagent grade ethanol, and blown dry with nitrogen. Uniform wettability with water after this treatment was considered a good indication of surface cleanliness. All experiments were carried out at a constant temperature of 30 °C, with the electrolytic solutions in equilibrium with the atmosphere (i.e., aerated solutions).

All chemicals with the exception of SDBS were of analytical reagent grade (Merck) and were used without further purification. Solutions were prepared using twicedistilled water. SDBS was obtained as a solid containing 80% active constituent (Merck), the remainder being sodium sulphate. Importantly, surfactant impurities were reported absent in the product.

The present study was conducted in sulphuric acid medium; the presence of a slight additional amount of sulphate ions believed to have no effect on the results. In preparing SDBS solutions the actual surfactant concentration in the starting material was taken into account by weighing 1/0.8 = 1.25 times the theoretical mass of pure SDBS.

2.2 Electrochemical impedance

Impedance measurements were carried out at the open circuit potential (E_{ocp}) , using a computer-controlled potentiostate (PAR EG&G Model 273A) and a 1,025 frequency response analyzer. In the conventional three-electrode assembly, a Pt foil auxiliary electrode and a saturated calomel reference electrode (SCE) were used. After immersion of the specimen, prior to the impedance measurement a stabilisation period of 30 min was observed, which proved sufficient for E_{ocp} to attain a stable value. The A.C. frequency range extended from 100 kHz to 10 mHz, a 5 mV peak-to-peak sine wave being the excitation signal. Data processing was based on a non-linear least squares fitting procedure as described elsewhere [18]. For this purpose, the Zview (II) software was used and for transforming constant phase element parameter values into values of idealized capacitances, a procedure outlined in the same reference was employed.

2.3 Tafel polarization measurements

The same equipment as for the impedance measurements was used leaving the frequency response analyser out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mV s⁻¹. All potentials are reported versus the saturated calomel reference electrode (SCE). Corrosion current densities were obtained from the polarisation curves by Tafel curve simulation using SoftCorr352 software. In this technique, potential is assessed at approximately ± 50 mV than open circuit potential (E_{ocp}). Correction of the curves for IR-drop was not required in view of the high electrical conductivity of the strongly acidic solutions.

3 Results and discussion

3.1 Tafel polarization measurements

Representative examples of Tafel polarization curves are shown in Fig. 1 and relevant parameter values are



Fig. 1 (**A**) Tafel polarization curves for copper in 0.5 mol dm⁻³ sulphuric acid without inhibitor and in the presense of the following concentration of SDBS (mol dm⁻³) (a) blank; (b) 10^{-5} ; (c) 5×10^{-5} ; (d) 10^{-4} ; (**B**) Tafel polarization curves for copper in 0.5 mol dm⁻³ sulphuric acid with 5×10^{-5} mol dm⁻³ 2-MBI and in the presence of the following concentrations of SDBS (in mol dm⁻³): (a)without SDBS; (b) 10^{-5} ; (c) 5×10^{-5} ; (d) 10^{-4} ; (e) 5×10^{-4}

summarized in Table 1 (corrosion current density $i_{\rm corr}$, corrosion potential $E_{\rm corr}$, anodic and cathodic Tafel slopes $\beta_{\rm a}$, $\beta_{\rm c}$, respectively). Table 1 further presents values of the corrosion inhibition efficiency, for which the expression in this case is:

$$\eta_{\%p} = \frac{i_{\text{corr}_0} - i_{\text{corr}}}{i_{\text{corr}_0}} \times 100 \tag{1}$$

where i_{corr} and i_{corr_0} are the corrosion current densities ($\mu A m^{-2}$) for the inhibited and uninhibited solutions, respectively.

In the presence of 2-MBI the value of the cathodic Tafel slope remains approximately unchanged as the composition of the corrosive medium is varied, which is a clear indication that the mechanism of the electron acceptor reaction does not change. However, in the presence of SDBS the cathodic slope changes significantly. Moreover, it is observed that the addition of SDBS does not change the corrosion potential, which is shifted in the noble direction upon addition of 2-MBI. Figure 2 presents inhibition efficiency values as a function of inhibitor concentration. For 2-MBI, a monotonic increase in $\eta_{\%p}$ is observed over the entire investigated concentration range (up to 5×10^{-4} mol dm⁻³). The slope of the $\eta_{\%p}$ curve gradually decreases with increasing 2-MBI concentration, which points to a simple adsorption behavior. Further information for this assumption is discussed in Sect. 3.3, dealing with adsorption isotherms.

The behavior resulting from the addition of SDBS is somewhat more intricate (curve b in Fig. 2), as a maximum in the inhibitive efficiency 63% is observed for concentrations around 3 \times 10⁻⁴ mol dm⁻³. An increase in C_{SDBS} beyond this value results in diminished corrosion protection. This phenomenon can be ascribed to the formation of so-called hemi-micelles. Curve c in Fig. 2 shows the effect of SDBS on the inhibition efficiency of 2-MBI (10^{-4}) mol dm⁻³ 2-MBI with different SDBS). At concentrations of surfactant close to or beyond the critical micelle concentration (*cmc*), the withdrawal of adsorbate back into the bulk solution probably becomes thermodynamically favorable. Although the cmc was not independently determined in the present investigation, analogy with the more studied sodium dodecylsulphate (SDS) suggests a value of the same order of magnitude, being 8×10^{-4} mol dm⁻³ for SDS in the current medium (H_2SO_4 0.5 mol dm⁻³) [19]. The fact that SDBS, due to the presence of a benzene ring in its structure, is bulkier than SDS is an indication that the cmc for SDBS can differ somewhat from the corresponding value for SDS.

Figure 3 presents values of synergism parameter, *s*, for all investigated concentrations of SDBS and 2-MBI. In order to judge whether synergism is taking place, one has to calculate the synergism parameter as initially proposed by Murakawa et al. [20] for describing the combined inhibition behavior of amines and halide ions.

Generally, for the interaction of inhibitors A and B, this synergism parameter is defined as follows:

$$s = \frac{1 - \eta_A - \eta_B + \eta_A \eta_B}{1 - \eta_{AB}} \tag{2}$$

where η_A and η_B are the inhibition efficiencies observed with compound A and B acting alone respectively, and η_{AB} is the experimentally observed inhibition efficiency for the mixture A + B (obviously, c_A and c_B in the mixture should be the same as in the corresponding separate situations).

The expression actually compares the theoretically expected corrosion rate (numerator), based on the known rates when either A or B are present and on the condition that they do not interact, with the experimentally observed rate in the presence of the inhibitor mixture (denominator). Consequently, in the case where inhibitors A and B have no effect on each other and are adsorbed at the metal/solution interface independently, s = 1. Alternatively, synergistic

Table 1Tafel polarisationparameters for the corrosion ofcopper in 0.5 M sulphuric acidin the presence of differentconcentration of SDBS and/or2-MBI

$\overline{C_{2-\text{MBI}}}$ (mol dm ⁻³) × 10 ⁵	C_{SDBS} (mol dm ⁻³) × 10 ⁵	<i>E</i> _{corr} (mV vs. SCE)	$i_{\rm corr}$ ($\mu A \ {\rm cm}^{-2}$)	$\eta_{\%p}$	$\beta_{\rm c} \ ({\rm mV} { m decade}^{-1})$	$\beta_a (mV)$ decade ⁻¹
0	0	-31	18		138.1	37.7
0	1	-31.4	13.5	25	201.5	36.8
0	5	-35	9.1	49	293.2	40.2
0	10	-32	6.6	63	247.5	41.12
0	50	-34	8.6	52	66.4	15.6
1	0	-21	4.5	75	114	45.1
1	1	-12.5	4.1	77	335	116
1	5	-11	3.2	82	151	40
1	10	-10	2.4	87	87.4	36
1	50	-9	3.2	82	77.7	43.86
5	0	15.8	4	78	128	37
5	1	16.4	2.8	84	74.5	56.82
5	5	16.2	2.4	87	63.5	27.8
5	10	14.9	1.4	92	54.08	44.03
5	50	19.6	2.1	88	73.6	29.65
10	0	30.5	3.2	82	74.1	35.1
10	1	33.4	2.8	84	56.5	25.94
10	5	30.43	1.6	91	76.5	42
10	10	34.36	0.81	96	57.4	34.56
10	50	33.13	1.1	94	98.23	60.1
50	0	33.2	1.3	93	63.3	38.2
50	1	31.1	1.6	91	40.2	40.2
50	5	32.5	1.4	92	43.7	34.6
50	10	32.3	1.3	94	46.3	36.1
50	50	33.1	1.3	93	70.2	52.43



Fig. 2 Corrosion inhibition efficiency of copper versus concentration in 0.5 sulphuric upon addition of : (a) SDBS; (b) 2-MBI and (c) 10^{-4} mol dm⁻³ 2-MBI with different SDBS (data fextraction rom Tafel measurment)

effects manifest themselves if s > 1 and antagonistic effects if s < 1. Figure 3 shows that below concentration of 5×10^{-5} mol dm⁻³ of SDBS and 10–4 mol dm⁻³ of 2-MBI, there is no synergism effect, but synergism is observed in the presence of concentrations of SDBA and 2-MBI above 10–4 mol dm⁻³.



Fig. 3 Synergism parameter *s* versus concentration of SDBS for the combined effect of SDBS and 10^{-4} mol dm⁻³ 2-MBI on the corrosion of copper in 0.5 mol dm⁻³ sulphuric acid

3.2 Electrochemical impedance

Typical impedance spectra for some selected SDBS concentrations are shown in Figs. 4 and 5 for the SDBS and 2-MBI and for SDBS alone. The spectra for SDBS alone were chosen as they clearly illustrate the optimum point in inhibition efficiency for a concentration of about 3×10^{-4} mol dm⁻³ after which the inhibition decreases.



Fig. 4 Complex plane plot for copper in 0.5 M sulphuric acid in the presence of the following SDBS concentration (in mol dm⁻³): (\bigcirc)without SDBS(Bare Metal) (\blacklozenge) 5 × 10⁻⁵;(×) 10⁻⁴; (\blacktriangle) 2 × 10⁻⁴; (\blacksquare) 3 × 10⁻⁴; (\blacklozenge) 4 × 10⁻⁴



Fig. 5 Complex plane plot for copper in 0.5 M sulphuric acid and 10^{-5} M SDBS in the presence of the following 2-MBI concentration(in mol dm⁻³): (a) without 2-MBI; (b) 5×10^{-5} ; (c) 10^{-4} ; (d) 2×10^{-4} ; (e) 3×10^{-4} ; (f) 4×10^{-4}

The main feature shown in the Fig. 5 spectra is obviously their semicircular appearance for combined SDBS with 2-MBI. In addition, this feature is observed when 2-MBI is used alone, independent of concentration. For the frequency range applied for these measurements, no indications of mass transport control were observed. Often, the observed behavior is modelled to a simplified Ershler– Randles circuit (i.e., with the Warburg impedance element omitted) [21].

Because the capacitance in corrosion phenomenon is not ideal, we prefer using a constant phase element (*CPE*), which has an impedance function of the following form:

$$Z_{cpe} = \frac{1}{Y_0(j\omega)^n} \tag{3}$$

where Y_0 and *n* are frequency-independent parameters and *n* is in the range $-1 \le n \le 1$. It is easily verified that *CPE* shows purely resistive, capacitive or inductive behaviour when n = 0, 1 or -1, respectively. Although a function of the above form allows very precise simulation of the measured impedance behaviour, the parameters Y_0 and *n* cannot immediately be interpreted as familiar electrical

parameter values. A possibility to overcome this problem, although not ideal, is based on the fact that a *CPE* as used here (i.e., replacing a capacitor in an equivalent circuit, with values of *n* somewhat below 1), points to processes not entirely conservative but partly dissipative (note that the charging and discharging of a physical capacitor are conservative processes). Formally, the conservative contribution to the observed *CPE*—behaviour can be isolated, and the result can be interpreted as an idealised capacitance value C_{id} . It was discussed previously that these idealised capacitance values can be calculated from cpe parameter values Y_0 and *n* using the expression [18]:

$$C_{id} = \frac{Y_0 \omega^{n-1}}{\operatorname{Sin}(n\frac{\pi}{2})} \tag{4}$$

where ω is the angular frequency for which the imaginary part of the impedance -Z'' reaches its maximum (corresponding with the apex of the arc in the complex plane). It can be shown that this value of the angular frequency can be calculated as [1]:

$$\omega_{-Z_{\text{Max}}''} = \left(\frac{1}{R_{ct}Y_0}\right)^{1/n} \tag{5}$$

Values of impedance parameters R_{cl} , Y_0 and n and of derived parameters C_{dl} (calculated as discussed) and $\eta_{\%Z}$ are presented in Table 2.

Figure 4 shows that both in the absence of inhibitor and presence SDBS the electrochemical behavior of electrode is controlled by diffusion (Warburg phenomenon).

Comparison between the data in Tables 1 and 2 shows that satisfactory agreement is found with the inhibition efficiencies as obtained through polarizations measurements and electrochemical impedance. Further, it is observed that the measured double layer capacitance decreases as inhibition is more efficient, i.e., as higher values of R_{ct} are calculated.

This phenomenon is commonly found in cases where adsorption at the metal/electrolyte interface occurs, as solvent molecules (in case water, with high dielectric constant) become replaced with molecules with far less pronounced dielectric properties. If molecular adsorption at the metal/solution interface is essentially the mechanism through which corrosion inhibition occurs, several adsorption isotherms can tested for their relevance in describing the interaction between inhibitor and metal surface at least on a phenomenological level.

3.3 Adsorption isotherms

Adsorption isotherms are very important in understanding the mechanism of organo-electrochemical reactions [22]. All the isotherms obey the general formula: Table 2 Impedance parametersfor the corrosion of copper in0.5 M sulphuric acid in thepresence of differentconcentration of SDBS and/or2-MBI

$\frac{C_{2-\text{MBI}}}{(\text{mol dm}^{-3}) \times 10^5}$	$\frac{C_{\rm SDBS}}{\rm (mol \ dm^{-3}) \times 10^5}$	R_{ct} ($\Omega \text{ cm}^2$)	$Y_0 \times 10^6$ ($\Omega^{-1} \text{ cm}^{-2}$)	n _{dl}	$\frac{C_{dl}}{(\mu F \text{ cm}^{-2})}$	$\eta_{\%z}$
0	0	120	262	0.82	128	
0	1	154	236	0.84	130	22.08
0	5	286	221	0.85	140	58.04
0	10	483	130	0.89	93	75.16
0	50	331	150	0.84	87	63.75
1	0	532	278	0.85	204	77.44
1	1	622	124	0.86	83.7	80.71
1	5	657	104	0.91	80.6	81.74
1	10	725	80	0.93	65	83.45
1	50	711	119	0.87	84	83.12
5	0	1,016	271	0.81	210	88.19
5	1	1,134	131	0.84	94	89.42
5	5	1,604	72	0.88	54	92.52
5	10	1,786	70	0.87	52	93.28
5	50	1,599	72	0.81	45	92.50
10	0	3,333	39	0.73	20.1	96.40
10	1	3,536	25	0.78	13.4	96.61
10	5	3,675	23	0.83	14.4	96.73
10	10	3,748	20	0.88	14.3	96.80
10	50	3,653	30	0.82	19.2	96.72
50	0	3713	42	0.81	28.4	96.77
50	1	3740	33	0.85	23.5	96.79
50	5	3735	27	0.91	21.7	96.79
50	10	3750	24	0.92	19.6	96.80
50	50	3740	32	0.91	26.2	96.79

$$f(\theta, x) \exp(-2a\theta) = Kc$$

(6)

where $f(\theta, x)$ is the configurationally factor, which depends upon the physical model and the assumptions underlying the derivation of isotherm [23] θ is the degree of surface coverage, x the size ratio, "a" the molecular interaction parameter, c is the inhibitor concentration in the electrolyte and K is the equilibrium constant of the adsorption process.

The simplest, the Langmuir isotherm, is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites. Under these circumstances the proportionality between surface coverage θ and bulk concentration c of the adsorbing compound is as follows:

Langmuir's adsorption isotherm:

$$\frac{c}{\theta} = c + \frac{1}{K} \tag{7}$$

As θ is a dimensionless quantity, the adsorption equilibrium constant *K* must have the inverse dimension of concentration, i.e., dm³ mol⁻¹. Therefore, a linear relationship is observed when c/θ is plotted as a function of *c*, with a slope ideally of unity.

If simple adsorptive behavior is assumed for SDBS and 2-MBI in the present study, the surface coverage (θ) can readily be calculated from Eq. 1 (In this case, the inhibition efficiency is equal to surface coverage: $\theta = \eta = \eta_{\%}/100$.).

In Fig. 6, the Langmuir relation is plotted for 2-MBI and SDBS. The expected linear relationship is well approximated in the case of 2-MBI (correlation coefficients R^2 equal to 0.993), and the line has a slope of 0.945. The deviation of the slope from unity is often interpreted as a sign that the adsorbing species occupy more or less than a typical adsorption site at the metal/solution interface [23].

In addition the experimental data was fitted to Temkin's adsorption isotherm. In Fig. 7, the Temkin relation is plotted for 2-MBI and SDBS.

Temkin's adsorption isotherm:

$$e^{-2a\theta} = Kc \tag{8}$$

Knowing that:

$$K = \exp(\frac{-\Delta G_{ads}^0}{RT}) \tag{9}$$

where, R is the universal gas constant and T the thermodynamic temperature. For 2-MBI the value of the free



Fig. 6 Langmuir adsorption isotherm plots of 2-MBI and SDBS on corrosion in 0.5 mol dm⁻³ sulphuric acid (key: (\blacklozenge) 2-MBI; (\blacksquare) SDBS up to 3 × 10⁻⁴ mol dm⁻³; (\blacktriangle) SDBS higher concentration than 3 × 10⁻⁴ mol dm⁻³

energy of adsorption, ΔG_{ads}^0 , determined from our experimental findings was $-25.9 \text{ kJ mol}^{-1}$.

A value of -40 kJ mol^{-1} is usually adopted as a threshold between chemi- and physisorption [24]. Thus the value found for 2-MBI on copper clearly indicates that the adsorption is of a physical-probably electrostatic- nature and that no covalent bond between inhibitor molecule and metal surface is established.

For SDBS, it must be kept in mind that the behavior profoundly changes at a concentration of about 3×10^{-4} mol m⁻³. For this reason, it was not surprising that no Langmuir behavior was found for $c_{\text{SDBS}} > 3 \times 10^{-4}$ mol dm⁻³ (for clarity, data points in Fig. 6 corresponding to the two concentration regions have been marked differently). For this inhibitor except for the lower concentrations linearity is met up to a certain extent, the severe deviation of the slope from unity (slop equal to 1.37) is a clear indication that also for $c_{\text{SDBS}} < 3 \times 10^{-4}$ mol dm⁻³, at least one of the criteria for applying the Langmuir formalism is not fulfilled. So for SDBS, adsorption, behavior cannot described using the Langmuir's adsorption isotherm.

The results for the Temkin isotherm for both 2-MBI and SDBS is displayed in Fig. 7. From this figure, it is found that the adsorption behavior of 2-MBI cannot be described using the Temkin isotherm (R^2 for 2-MBI is 0.851).

For SDBS, again disregarding the data points for concentrations above 3×10^{-4} mol dm⁻³, the Temkin isotherm proved to be considerably more successful than the Langmuir equivalent in describing the behavior $(R^2 = 0.991$ for the linear relation shown in Fig. 7). The value of the relevant quantity in this case is: $\Delta G_{ads}^0 = -34.46$ kJ mol⁻¹. Consequently, the adsorption



Fig. 7 Temkin isotherm plots for 2-MBI and SDBS on corrosion in 0.5 mol dm⁻³ sulphuric acid (key: (\blacklozenge) 2-MBI; (\blacksquare) SDBS up to 3 × 10⁻⁴ mol dm⁻³; (\blacktriangle) SDBS higher concentration than 3 × 10⁻⁴ mol dm⁻³

reactions are exothermic as in the cases of 2-MBI and SDBS. Therefore, we can suggest that the adsorption of the inhibitors on the electrode is by physisorption.

4 Conclusions

EIS and Tafel polarization measurements were employed to increase knowledge of the corrosion of copper in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; the inhibitive effect of a scarcely studied anionic surfactant (SDBS) and the effect of combining it with a well-known 2-MBI was investigated. When SDBS is used alone as corrosion inhibitor, the inhibition efficiency shows a maximum at a concentration of about 3×10^{-4} mol dm⁻³. Upon mixing SDBS and 2-MBI, a slight antagonistic effect is observed if one of the additives is present in a concentration below 5×10^{-5} mol dm⁻³. However, at higher concentrations, this trend is reversed and a moderate synergism found. The adsorption of 2-MBI can be described using the Langmuir isotherm, which clearly fails in the case of SDBS. Adsorption of SDBS can be described using the Temkin isotherm. Values for ΔG_{ads}^0 indicate that, for both inhibitors, interaction with the metal surface is of a physical nature.

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References

- 1. Hosseini MG, Mertens SFL, Arshadi (2003) Corros Sci 45:473
- Hosseini MG, Mertens SFL, Ghorbani M, Arshadi MR (2003) Mater Chem Phys 78:800

- 3. Arshadi MR, Hosseini MG, Ghorbani M (2002) Br Corros J 37:76
- 4. Hosseini MG, Ehteshamzade M, Shahrabi T (2007) Electrochim Acta 52:3680
- Ehteshamzade M, Shahrabi T, Hosseini MG (2006) Appl Surf Sci 252:2949
- Ehteshamzade M, Shahrabi T, Hosseini MG (2006) Anti-Corros Methods Mater 53:147
- 7. Hosseini MG, Shahrabi T, Tavakholi H (2007) Anti-Corros Methods Mater 54:308
- 8. Singh DDN, Singh TB, Gaur B (1995) Corros Sci 37:1005
- 9. Villamil RFV, Corio P, Rubim JC, Agostinho SML (2002) J Electroanal Chem 535:75
- 10. Altura D, Nobe K (1972) Corrosion 28:345
- 11. Costa SLFA, Agostinho SML (1989) Corrosion 45:472
- 12. Makhhuf MTh, El-Shatory SA, El-Said A (1996) Mater Chem Phys 43:76
- 13. Wang L (2001) Corros Sci 43:2281
- 14. Assouli B, Srhiri A, Idrissi H (2004) Corrosion 60:399
- Hosseini MG, Shahrabi T, Nichols RJ (2005) Iranian J Sci Technol Trans A: Sci 29:49

- Doneux T, Buess-Herman C, Hosseini MG, Nichols RJ, Lipkpweski J (2005) Electrochim Acta 50:4275
- Hosseini MG (2002) Study of adsorption of 2-mercaptobenzimidazole on Cu(111) by electrochemical impedance spectroscopy and polarisation modulation infrared reflection—absorption spectroscopy. In: 53rd Annual meeting international society of electrochemistry. Dusseldorf, Germany
- Mertens SF, Xho C, De Cooman BC, Temmerman E (1997) Corrosion 53:381
- Villamil RFV, Corio P, Rubim JC, Agostinho SML (1999) J Electroanal Chem 472:112
- 20. Murakawa T, Nagaura S, Hackerman N (1967) Corros Sci 7:79
- 21. Randles JEB (1947) Discuss Faraday Soc 1:11
- 22. Bockris JOM, Khan SUM (1993) Surface electrochemistry. A molecular level approach, Plenum, New York
- 23. Ateya B, El-Anadouli B, El-Nizamy F (1984) Corros Sci 24:509
- Atkins PW (1999) Physical Chemistry, 6th edn. Oxford University Press