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Adsorption Mechanism of Eco-Friendly Corrosion Inhibitors for Exceptional Corrosion Protection of Carbon Steel: Electrochemical and First-Principles DFT Evaluations

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Synthesis of inhibitor molecules

The title compounds described here were synthesized according to the literature procedures [17]. Briefly, an equimolar mixture of thiazolidine-2,4-dione (**1**) (0.12 g, 1 mmol), 4-methoxylbenzaldehyde (**2a**) or 4-methylbenzaldehyde (**2b**) (1 mmol) in water/ethanol (v/v, 2:1) (10 ml) was treated with sodium hydroxide (1.1 mmol) at 5°C, then stirred for 5-6 h at room temperature (Scheme 1). The completion of the reaction was monitored by TLC. The reaction mixture was acidified with diluted HCl. The solid was filtered and recrystallized from ethanol to give pure product MeOTZD and MeTZD. Their characterization is reported in supplementary material.

Synthesis of 5-(4-methoxybenzylidene) thiazolidine-2,4-dione (MeOTZD).

White solid, Yield = 92%. mp= 216-218°C (EtOH); TLC (cyclohexane–AcOEt: 70–30), Rf = 0.33; ^{1}H NMR (200 MHz, DMSO-d_6) δ (ppm) = 12.48 (s, 1H), 7.67 (s, 1H), 7.47 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (50 MHz, DMSO) δ (ppm) = 167.88, 167.34, 160.88, 131.99 x 2, 131.75, 125.39, 120.15, 114.78 x 2, 55.37; MS (ESI$^+$): m/z = 236.4 [M+H]$^+$.

Synthesis of (Z)-5-(4-methylbenzylidene) thiazolidine-2,4-dione (MeTZD).

White solid, Yield = 50%; mp 229-231°C; TLC (cyclohexane–AcOEt: 70–30), R_f = 0.46 ;^{1}H NMR (200 MHz, DMSO-d_6) δ, ppm (J, Hz): 12.56 (1H, s, NH); 7.73 (1H, s, ArCH=C); 7.46 (2H, d, J = 4.4 Hz,H Ar); 7.32 (2H, d, J = 4.4 Hz, H Ar); 2.33 (3H, s, CH_3). ^{13}C NMR (50 MHz, DMSO) δ, ppm: 167.8 (C=O); 167.3 (C=O); 140.6 (<u>C</u>H=C); 131.8 (C-4 Ar); 130.2 (C-1 Ar); 130.0 (C-2 Ar); 129.8 (C-3 Ar); 122.2 (C-5 TZD); 21.0 (CH_3). MS (ESI$^+$): m/z = 220.2 [M+H]$^+$.

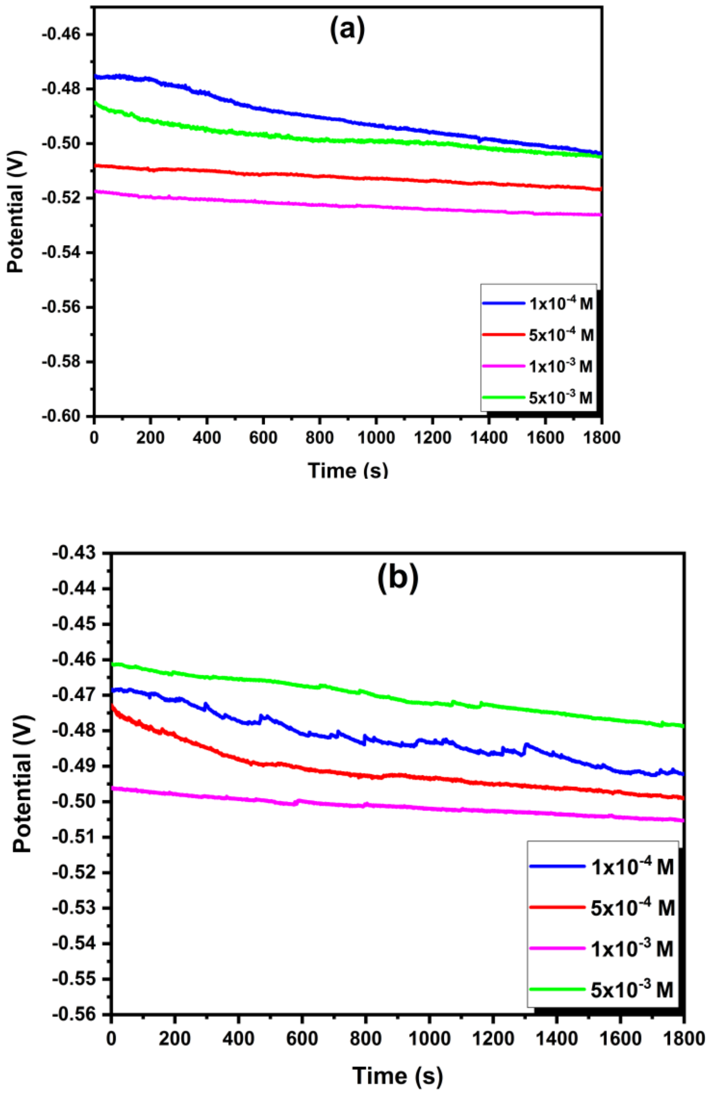

Figure S1. The variation of open circuit potential as function of time of MeOTZD (a) and MeTZD (b).

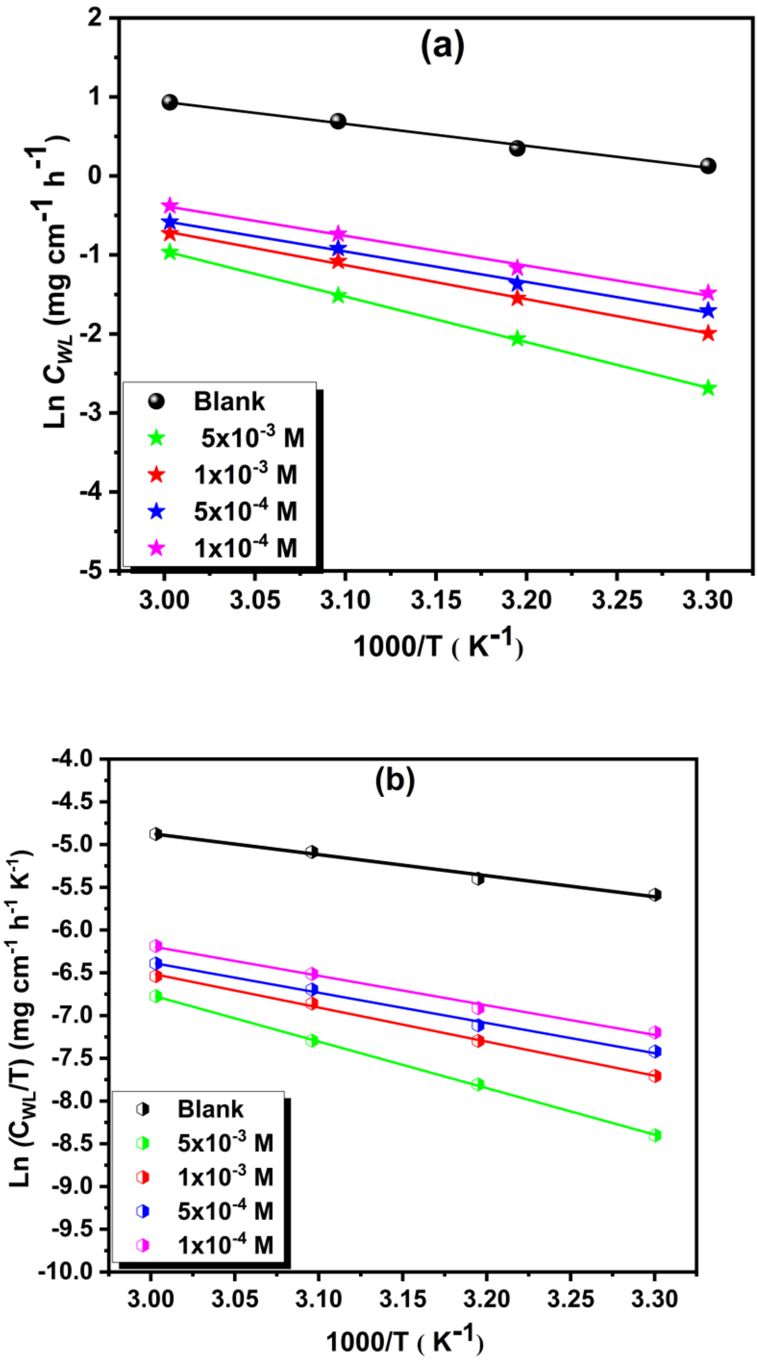

Figure S2. Arrhenius (a) and transition state (b) plots for corrosion inhibition of carbon steel in absence and presence of different concentrations of MeOTZD in 1.0 M HCl.

Table S1. MeOTZD activation parameters.

	Blank	**MeOTZD**			
		5×10^{-3}	**1×10^{-3}**	**5×10^{-4}**	**1×10^{-4}**
E_a ($kJmol^{-1}$)	23.126	47.9021	35.7905	32.031	31.3909
ΔH_a ($kJmol^{-1}$)	20.488	45.2629	33.1513	29.3917	28.7516
ΔS_a ($Jmol^{-1}K^{-1}$)	-176.49	-117.87	-152.1	-162.32	-162.65

E_a - ΔH_a ($kJmol^{-1}$)	43.614	2.63928	2.6392	2.63928	2.63928

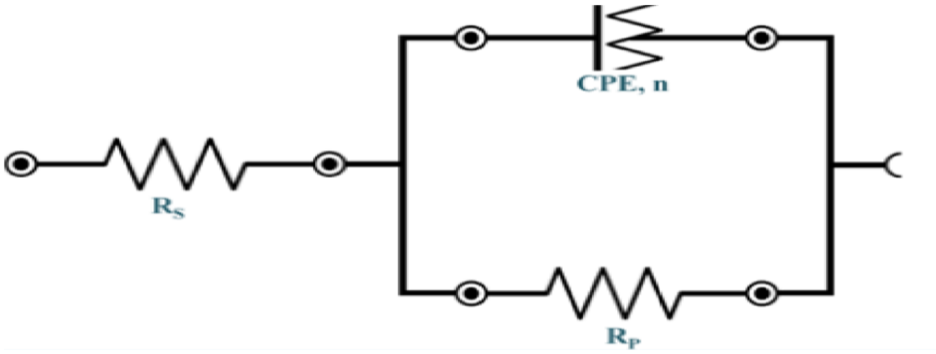

Figure S3. Equivalent circuit model applied to fit and simulate the impedance data.

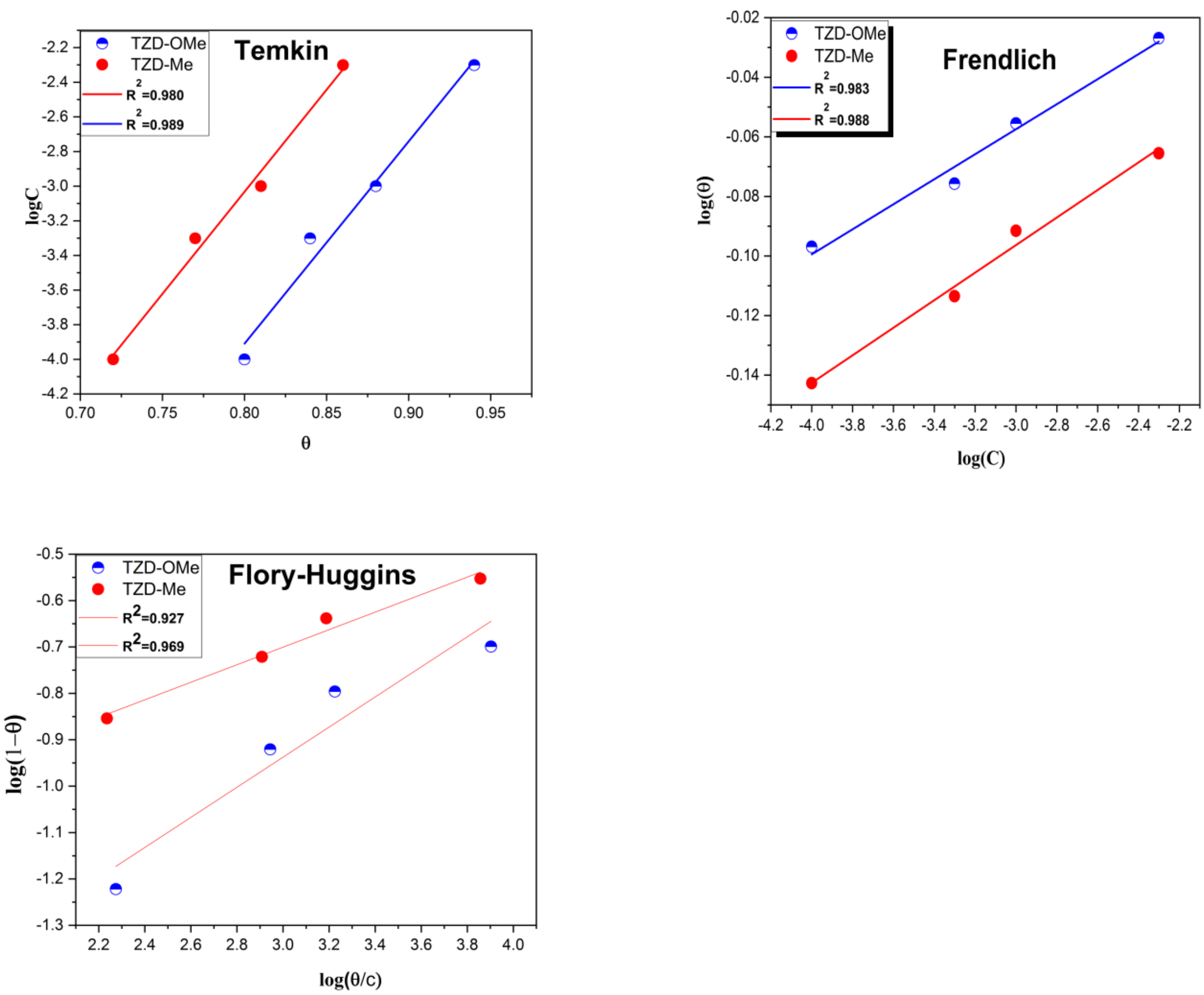

Figure 4. S: Isotherm plots for carbon steel in1.0 M HCl medium at 303 K containing different concentrations of MeOTZD and MeTZD.