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Fatty acid oxadiazoles as corrosion inhibitors for mild steel in formic acid

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Abstract

Selected oxadiazoles of fatty acids; namely 2-hepta decene-5-mercapto-1-oxa-3,4-diazole (HMOD); 2-undecane-5-mercapto-1-oxa-3,4-diazole (UMOD); and 2-decene-5-mercapto-1-oxa-3,4-diazole (DMOD), were synthesized. Their influence on the inhibition of corrosion of mild steel in 20% formic acid (HCOOH) was investigated by weight loss and potentiodynamic polarization techniques. The inhibition efficiency of the compounds was found to vary with concentration, immersion time and temperature. All the compounds showed good inhibition efficiency (e_{IE}) in formic acid solution. Adsorption on mild steel obeyed the Langmuir adsorption isotherm. Potentiodynamic polarization revealed that all three inhibitors, HMOD, UMOD, and DMOD are mixed inhibitors. Electrochemical impedance spectroscopy was also used to investigate the inhibition mechanism.

1. Introduction

Organic acids are widely used in the chemical industries and form a base for manufacturing various chemicals, drugs, plastics and fibers. Formic acid is the most corrosive of the common organic acids. Corrosion inhibition studies on metals in organic acid solutions are scarce in comparison with similar studies in mineral acids [1–4]. Mild steel has many uses in industry, as in the fabrication of reaction vessels, storage tanks, etc. which either manufacture or use formic acid as reactant.

Most of the effective organic inhibitors used contain heteroatoms such as O, N, S and multiple bonds in their molecules through which they adsorb on the metal surface. Corrosion inhibitors derived from fatty acid constitute an important potential class of corrosion inhibitors. Badran et al. investigated the corrosion-inhibiting property of a epoxidized linseed oils and oleic acid with methyl, ethyl, and butyl amines and reported >90% inhibition efficiency (e_{IE}) of these compounds in 0.05 M hydrochloric acid solution [5, 6]. Hanna et al. studied the inhibitive action of ethoxylated fatty acid derivatives as corrosion inhibitors for mild steel (MS) in HCl and sulfuric acid [7].

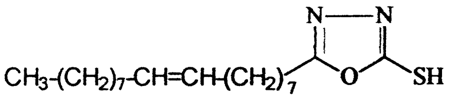
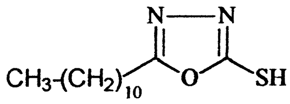
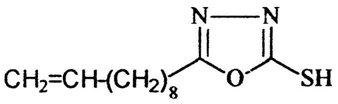
In continuation of our work on development of fatty acid derivatives as corrosion inhibitors [8–10], the authors have studied the corrosion inhibiting behaviour of fatty acid oxadiazoles, namely 2-hepta decene-5-mercapto-1-oxa-3,4-diazole (HMOD), 2-undecane-5-mercapto-1-oxa-3,4-diazole (UMOD), 2-decene-5-mercapto-1-oxa-3,4-diazole (DMOD) on the corrosion of MS in 20% formic acid solution.

2. Experimental details

Weight loss experiments were performed with cold-rolled mild steel samples of size 2 × 2.5 × 0.25 cm having composition (wt%): 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P and balance Fe as per ASTM [11]. The experiments were performed as described earlier [12]. Formic acid (MERCK) of AR grade was used to prepare solutions. Double-distilled water was used to prepare 20% solutions. The oxadiazoles of fatty acid were synthesized as described by Chande et al. [13] and characterized by their infrared spectra; purity was checked by thin-layer chromatography. Names and molecular structures of the compounds are given in Table 1.

Potentiodynamic polarization studies were carried using an EG&G PARC potentiostat/galvanostat (model 173), a universal programmer (model 175) and an X–Y recorder (model RE 0089). A platinum foil was used as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode; mild steel was used as the working electrode. All the experiments were carried out at a constant temperature of 26 ± 2 °C and a scan rate of 1 mV s^{-1} at o.c.p. The polarization curves were obtained after immersion of the electrode in the solution until a steady state was reached.

Table 1. Name and structural formula of the fatty acid oxdiazoles

S. No.	Structure	Designation and abbreviation
1.		**2-heptadecene-5-mercapto -1-oxa--3,4-diazole (HMOD)**
2.		**2-undecane-5-mercapto -1-oxa- 3,4 – diazole (UMOD)**
3.		**2-decane-5-mercapto -1-oxa-3,4 -diazole (DMOD)**

Impedance measurements were performed for the mild steel in 20% formic acid at 26 ± 2 °C in the absence and presence of 100 and 500 ppm of DMOD at the corrosion potential E_{corr} with an alternating a.c. voltage amplitude of 5 mV in the frequency range 5 Hz–100 kHz. A time interval of a few minutes was given for the open circuit potential o.c.p. to read a steady value. All the measurements were carried out with an EG&G PAR (model 273A) potentiostat/galvanostat, and an EG&G (PAR model 5301A) lock-in-amplifier using an IBM computer.

3. Results and discussion

3.1. *Weight loss studies*

Figure 1(a) show the variation of inhibition efficiency with inhibitor concentration. The inhibition efficiency was obtained from weight loss measurements at different oxadiazole concentrations at 30 °C. The percentage inhibition efficiency (e_{IE}) and surface coverage (θ) of each concentration were calculated using the following equations:

$$e_{\mathrm{IE}} = \frac{r_{\mathrm{o}} - r}{r_{\mathrm{o}}} \times 100 \qquad (1)$$

$$\theta = \frac{r_{\mathrm{o}} - r}{r_{\mathrm{o}}} \qquad (2)$$

where r_{o} and r are the corrosion rates in the absence and presence of inhibitors, respectively. The inhibition efficiency for all the compounds increases with increase in concentration. The maximum e_{IE} of each compound was achieved at 500 ppm and a further increase in concentration showed no appreciable change in inhibitor performance (Table 2). Every et al. [14] and Schmitt [15] reported that, often, a mixture of nitrogen and sulphur compounds are better corrosion inhibitors than either type alone. The compounds studied contain both nitrogen and sulphur atoms; hence they exhibit good performance ($e_{\mathrm{IE}} \geq 98\%$) on the corrosion of mild steel in 20% formic acid.

The variation of inhibition efficiency with increase in acid concentration is shown in Figure 1(b). It is clear that these compounds are good corrosion inhibitors, providing greater than 90% inhibition efficiency over the acid range 10–30%.

The variation of inhibition efficiency of all the three fatty acid triazoles with immersion time is shown in Figure 1(c). Increase in immersion time from 24 to 96 h gives no significant change in inhibition efficiency of UMOD and DMOD, while in HMOD there is a decrease in efficiency with time.

The influence of temperature on inhibition efficiency is shown in Figure 1(d). The inhibition efficiency for all the oxadiazoles decreases slightly with increase in temperature from 30 °C to 50 °C. The decrease in efficiency with temperature may be attributed to desorption of the inhibitor molecules from the metal surface at higher temperature.

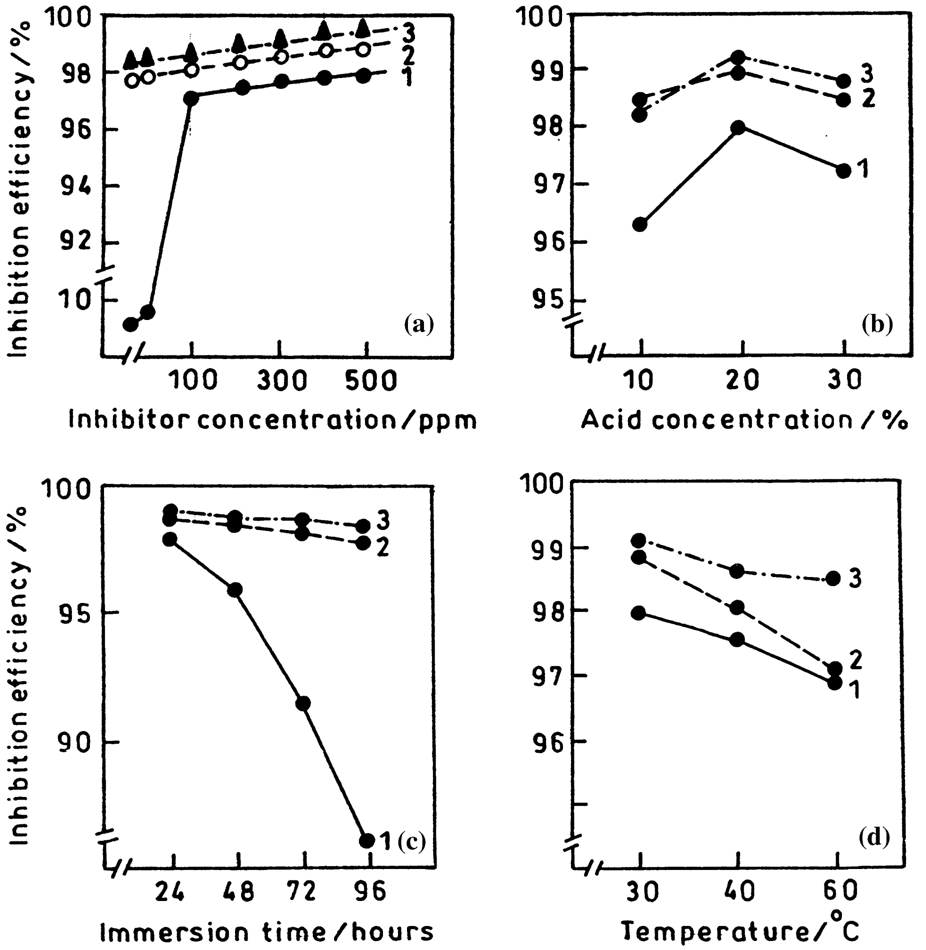


Fig. 1. Variation of inhibition efficiency with: (a) inhibitor concentration, (b) acid concentration, (c) immersion time and (d) solution temperature, in 20% formic acid for (1) HMOD; (2) UMOD; (3) DMOD.

The values of activation energy (E_a) were calculated using the Arrhenius equation [16, 17].

$$\ln\left(\frac{r_2}{r_1}\right) = -\frac{E_a \Delta T}{R T_1 T_2} \tag{3}$$

where, r_1 and r_2 are corrosion rates at temperature T_1 and T_2 respectively, $\Delta T = T_2 - T_1$. The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the equation:

$$\Delta G_{ads} = -RT \ln(55.5K) \tag{4}$$

and K is given by:

$$K = \theta / C(1 - \theta) \tag{5}$$

where θ is degree of coverage on the metal surface, C is the concentration of inhibitor in (mol l^{-1}) and K is equilibrium constant. The values of E_a and ΔG_{ads} are given in Table 3. The E_a values for inhibited systems are higher than those of uninhibited systems, indicating that all the inhibitors are more effective at room temperature [18]. The low and negative values of free energy of adsorption (ΔG_{ads}) indicate spontaneous adsorption and strong interaction of the inhibitor molecule with the mild steel surface [19, 20].

3.2. *Adsorption isotherm*

The mechanism of inhibition depends on the adsorption behavior of the organic adsorbate on the metal surface. Figure 2 shows the linear dependence of log (θ/(1−θ)) as a function of log concentration C of inhibitor, where θ is the surface coverage determined by using corrosion rate (*CR*). Inhibitor molecules adsorb on the metal surface according to the Langmuir isotherm model, which obeys the relation

$$\left(\frac{\theta}{1-\theta}\right) = kC \exp(-\Delta G_{ads}/RT) \tag{6}$$

ΔG_{ads} is the free energy of adsorption and C is the inhibitor concentration.

3.3. *Poteniodynamic polarization studies*

Potentiodynamic anodic and cathodic polarization scans were carried out in 20% formic acid for different fatty acid triazoles at 26 ± 2 °C. The various electrochemical parameters calculated from Tafel plots are given in Table 4. The lower corrosion current density (I_{corr}) values in the presence of the oxadiazoles without

Table 2. Corrosion parameter for mild steel in 20% formic acid in the absence and presence of different concentrations of various inhibitors from weight loss measurements at 30 °C for 24 h

Concentration/ppm	Weight loss/mg	IE/%	CR/mm y^{-1}
Blank	308.1	–	14.31
HMOD			
25	10.70	65.26	4.97
50	9.57	68.97	4.44
100	0.90	97.06	0.42
200	0.75	97.48	0.35
300	0.66	97.83	0.31
400	0.62	97.95	0.29
500	0.60	98.00	0.28
UMOD			
25	0.71	97.69	0.33
50	0.62	97.97	0.29
100	0.55	98.20	0.26
200	0.43	98.60	0.20
300	0.36	98.81	0.17
400	0.34	98.88	0.16
500	0.32	98.95	0.15
DMOD			
25	0.56	98.18	0.26
50	0.51	98.34	0.23
100	0.41	98.67	0.19
200	0.36	98.81	0.17
300	0.34	98.88	0.16
400	0.30	99.02	0.14
500	0.24	99.23	0.11

Table 3. Activation energy (E_a) and free energy of adsorption (ΔG_{ads}) for mild steel in 20% formic acid in the absence and presence of 500 ppm of various inhibitors

System	E_a/kJ mol^{-1}	-ΔG_{ads}/kJ mol^{-1}		
		30 °C	40 °C	50 °C
20% Formic acid	51.24	–	–	–
HMOD	70.47	36.82	37.24	37.95
UMOD	71.31	3628	38.83	39.21
DMOD	61.40	38.74	39.58	40.37

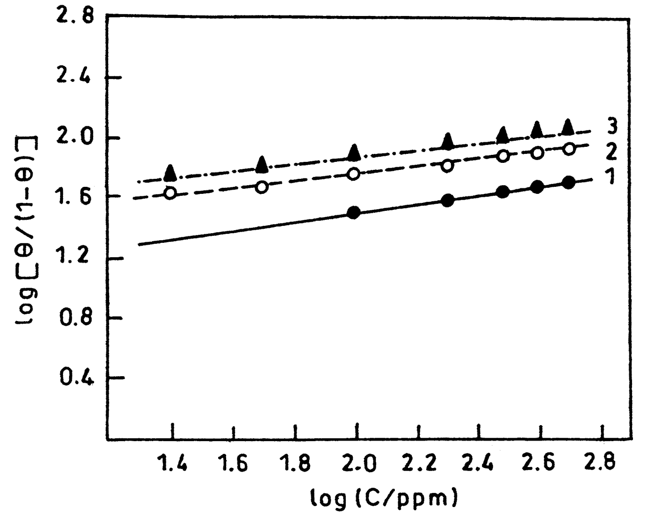


Fig. 2. Langmuir's adsorption isotherm plot for the adsorption of various inhibitors in 20% formic acid, on the surface of mild steel (1) HMOD; (2) UMOD; (3) DMOD.

Table 4. Electrochemical polarization parameters for the corrosion of mild steel in 20% formic acid containing 500 ppm of various inhibitors

System	E_{corr}/mV	b_a/mV decade^{-1}	b_c/mV decade^{-1}	I_{corr}/mA cm^{-2}	e_{IE}/%
20% Formic acid	−416	68	104	0.350	
HMOD	−418	62	120	0.091	74.00
UMOD	−420	72	114	0.090	74.28
DMOD	−422	72	112	0.060	82.85

Table 5. Electrochemical impedance parameters for mild steel in 20% formic acid containing different concentration of DMOD

Concentration/ppm	R_t/Ωcm^2	C_{dl}/μF cm^{-2}	e_{IE}/%
20% Formic acid	75.00	1862.09	–
DMOD			
100	1144.44	276.17	93.30
500	1211.11	258.22	93.69

causing significant changes in corrosion potential (E_{corr}), b_a (anodic Tafel slope) and b_c (cathodic Tafel slope), suggests that they are mixed type inhibitors (Figure 3). Maximum decrease in I_{corr} was observed for DMOD, indicating that DMOD (2-decene-5-mercapto-1-oxa-3,4-diazole) is the most effective corrosion inhibitor among those studied.

3.4. *Electrochemical impedance studies*

The electrical equivalent circuit for the system is shown in Figure 4. Impedance diagrams obtained for the frequency range 5 Hz–100 kHz at E_{corr} for mild steel in 20% formic acid are shown in Figure 5(a) and (b). The impedance diagrams are not perfect semicircles, and this difference has been attributed to frequency dispersion [21]. The values of chargetransfer resistance (R_t) and double-layer capacitance (C_{dl}) can be evaluated using the Nyquist and Bode plots [22]. The percentage e_{IE} was calculated using the Equation:

$$e_{IE}\frac{(1/R_{t0}) - (1/R_{ti})}{(1/R_{t0})} \times 100 \qquad (7)$$

where R_{t0} and R_{ti} are the charge transfer resistance without and with inhibitor, respectively, and are given in Table 4. Values of R_t increases with increase in inhibitor concentration (DMOD) and this in turn leads to an increase in e_{IE}. The addition of DMOD to 20% formic acid lowers the C_{dl} values, suggesting that the inhibition can be attributed to surface adsorption of the inhibitor [9].

3.5. *Mechanism of corrosion inhibition*

The corrosion of mild steel in formic acid solution may be considered in the following steps [4]:

$$Fe + HCOO^- \longrightarrow [Fe(HCOO)]_{ads} + e^- \qquad (8)$$

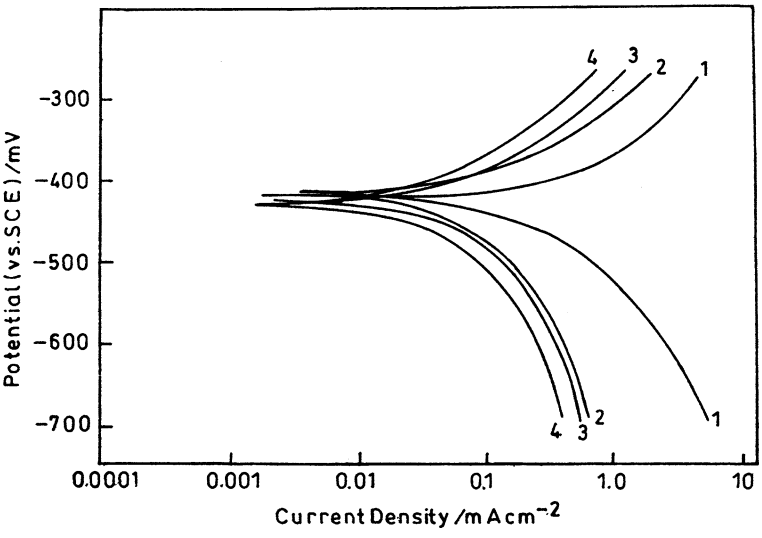


Fig. 3. Potentiodynamic polarization curves for the corrosion of mild steel in 20% formic acid in the absence and presence of 500 ppm of various inhibitors (1) Blank; (2) HMOD; (3) UMOD; (4) DMOD.

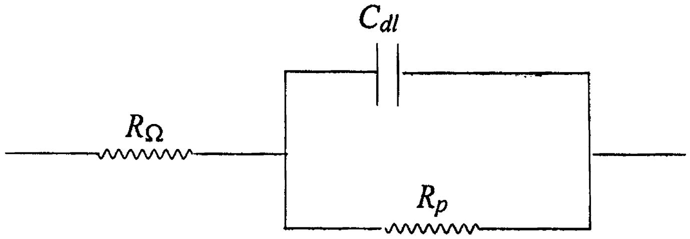


Fig. 4. Electrical equivalent circuit for the system (R: = uncompensated resistance, R_p = polarization resistance, C_{dl} = double layer capacitance).

$$[\mathrm{Fe(HCOO)}]_{\mathrm{ads}} \longrightarrow [\mathrm{Fe(HCOO)}]^{+} + e^{-} \qquad (9)$$

$$[\mathrm{Fe(HCOO)}^{+} + \mathrm{H} \rightleftharpoons \mathrm{Fe}^{+} + \mathrm{HCOOH} \qquad (10)$$

The evolution of hydrogen occurs as the cathodic reaction by the following mechanism:

$$\mathrm{M} + \mathrm{HCOOH} + e^{-} \longrightarrow \mathrm{MH}_{\mathrm{ads}} + \mathrm{HCOO}^{-} \qquad (11)$$

$$\mathrm{MH}_{\mathrm{ads}} + \mathrm{MH}_{\mathrm{ads}} \rightarrow \mathrm{H}_2 + \mathrm{M} \qquad (12)$$

The adsorption of formate ions on iron is a prerequisite for the anodic dissolution to occur; thus the rate of corrosion should depend on the concentration of formate ion in the solution. The conductance of formic acid solution gradually increases in the concentration range 5–20%. As a result the extent of adsorption of formate ion, as well as the rate of step (7), increases and consequently the rate of corrosion also increases.

The effectiveness of a compound depends on its structure. Inhibition of corrosion of mild steel in acidic solution by fatty acid oxadiazoles can be explained on the basis of molecular structure. It is apparent from the molecular structures that these compounds are able to adsorb on the metal surface through π-electrons of the aromatic ring and the lone pair of electrons of N, O and S atoms [23]. The difference in inhibition efficiency of HMOD, UMOD, and DMOD can be explained on the basis of their molecular structure. DMOD showed better performance than UMOD due to the presence of the polar group, as well as through π-electrons of the double bond. HMOD showed lowest inhibition efficiency, because it contains more than 10 carbon atoms [24].

4. Conclusions

All the fatty acid oxadiazoles performed excellently as corrosion inhibitors for mild steel in formic acid. They inhibited corrosion by an adsorption mechanism and the adsorption follows the Langmuir adsorption isotherm. All the oxadiazoles examined acted as mixed type inhibitors.

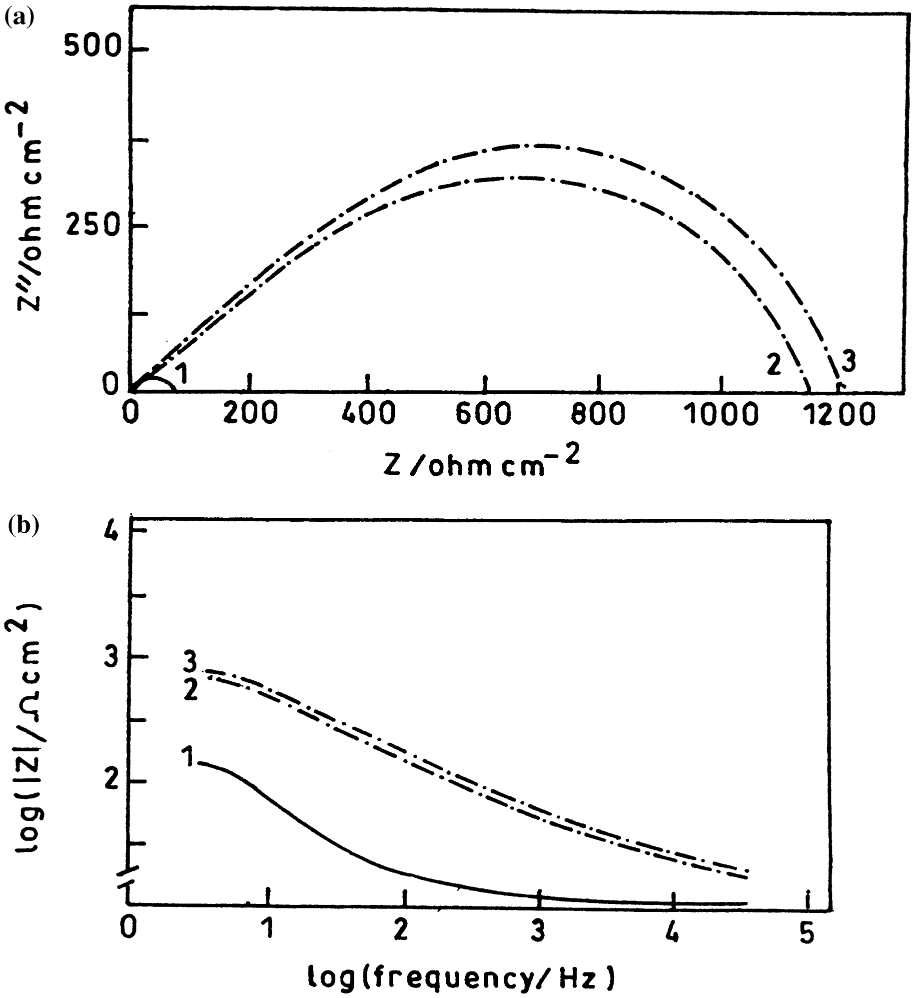


Fig. 5. (a) Nyquist plot and (b) Bode plot for mild steel in the absence and presence of various concentrations of DMOD (1) Blank; (2) 100 ppm; (3) 500 ppm.

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