

# Supporting Information

## Influence of Hydroxyl Groups on the Inhibitive Corrosion of Gemini Surfactant for Carbon Steel

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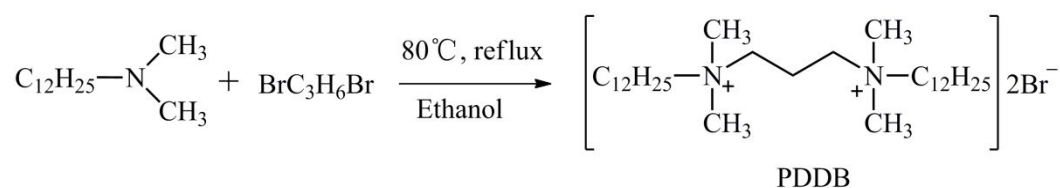
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## Experimental

### Synthesis of propanediyl-1,3- bis(*N,N*-dimethyl-*N*-dodecylammonium bromide) (PDDB)

In this work, the synthesis of PDDB was similar to the procedure reported by Zana et al.<sup>1</sup> In brief, 0.22 mol dimethyldodecylamine and 0.1 mol 1,3-dibromopropane were added in a round flask with a capacity of 250 mL and 150 mL absolute ethanol was added as solvent. Herein, in order to ensure the complete biquaternization as much as possible, a 10% excess of dimethyldodecylamine was adopted. This reaction was performed under reflux for 48 h at  $T = 80\text{ }^{\circ}\text{C}$ , as shown in Scheme 1. The final product of PDDB was obtained via recrystallizing in absolute ethanol/ethyl acetate mixed solvent at least three times. The chemical structure of PDDB was characterized by Fourier Transform infrared (FT-IR), given in Figure S1 and  $^1\text{H}$  (Figure S2) and  $^{13}\text{C}$  (Figure S3) nuclear magnetic resonance (NMR) spectra.



**Scheme S1. Synthesis routes of PDDB**

### Synthesis of propanediyl-1,3- bis(*N,N*-dihydroxyethyl-*N*-dodecylammonium bromide) (PDHDB)

PDHDB was synthesized using a modified method reported by Wang et al.,<sup>2</sup> as shown in Scheme 2. Briefly, 0.4 mol diethanolamine and 0.1 mol dodecylbromide were firstly added in a round flask and 100 mL *iso*-propanol was added as solvent. This reaction was conducted under stirring at  $50\text{ }^{\circ}\text{C}$  for 48 h. Then, the solvent was removed by rotatory evaporation and dried in vacuo for 24 h under  $50\text{ }^{\circ}\text{C}$ , and the crude product was extracted using a petroleum ether or diethyl ether and water system, where the organic phase was retained. After that, the organic solvent was removed by rotatory evaporation and dried in vacuum for 24 h under  $50\text{ }^{\circ}\text{C}$ , affording *N,N*-dihydroxyethyl-dodecylamine with a yield of 79.6%. Finally, 0.22 mol of *N,N*-



water centered at about  $3430\text{ cm}^{-1}$ . FT-IR spectra of PDHDB were similar to the characteristic peaks of PDDB, apart from three typical bands:  $\nu$  (O–H involved in hydroxyl) at  $\sim 3300\text{-}3288\text{ cm}^{-1}$ ,  $\delta$  (O–H) at  $1380\text{ cm}^{-1}$  (in plane) and  $\nu$  (C–O) at  $1080\text{ cm}^{-1}$ .

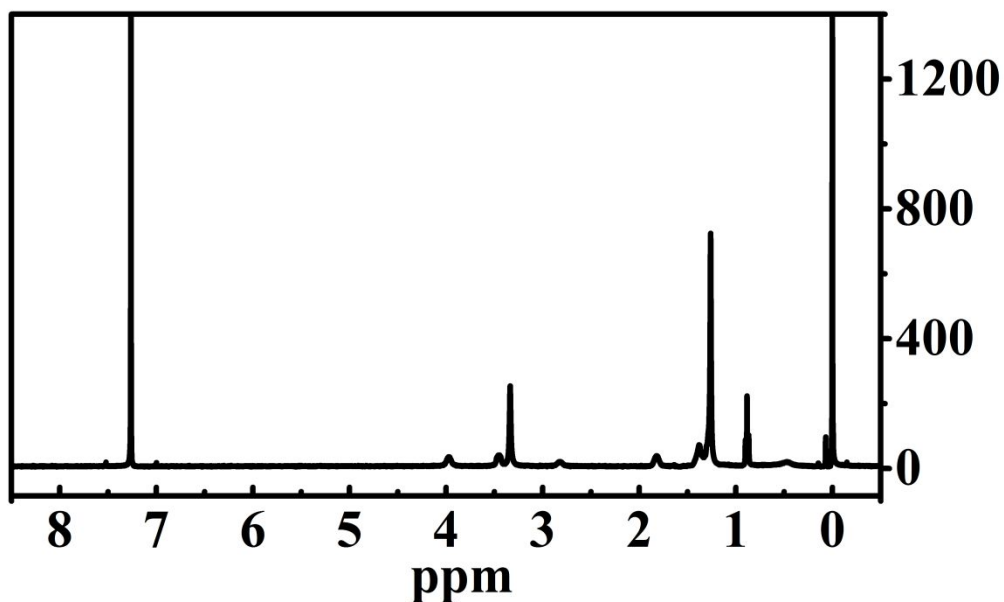


Figure S2. The  $^1\text{H}$  NMR spectra of PDDB

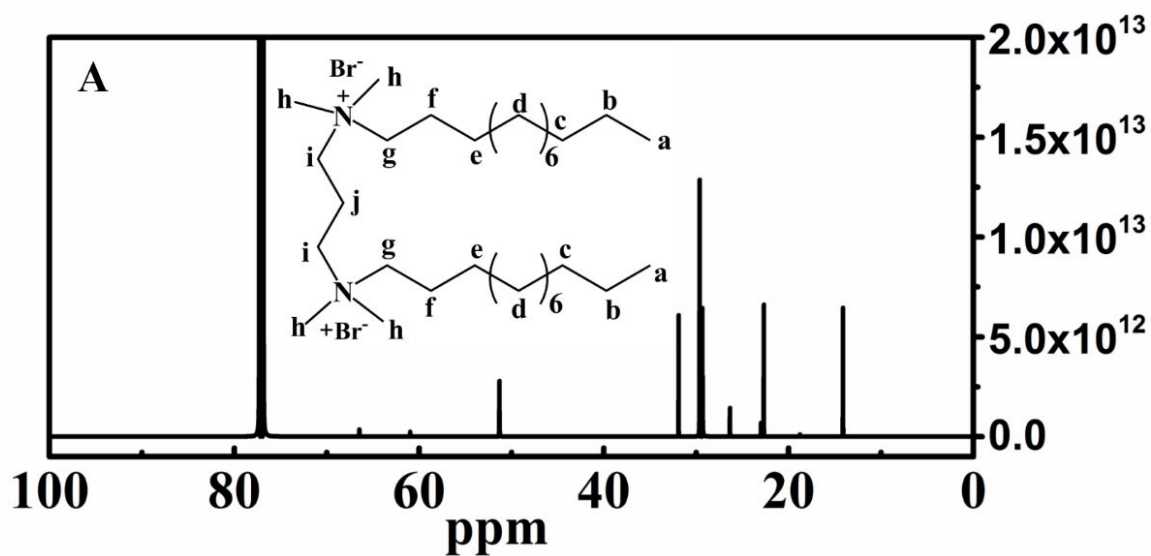


Figure S3. The  $^{13}\text{C}$  NMR spectra of PDDB

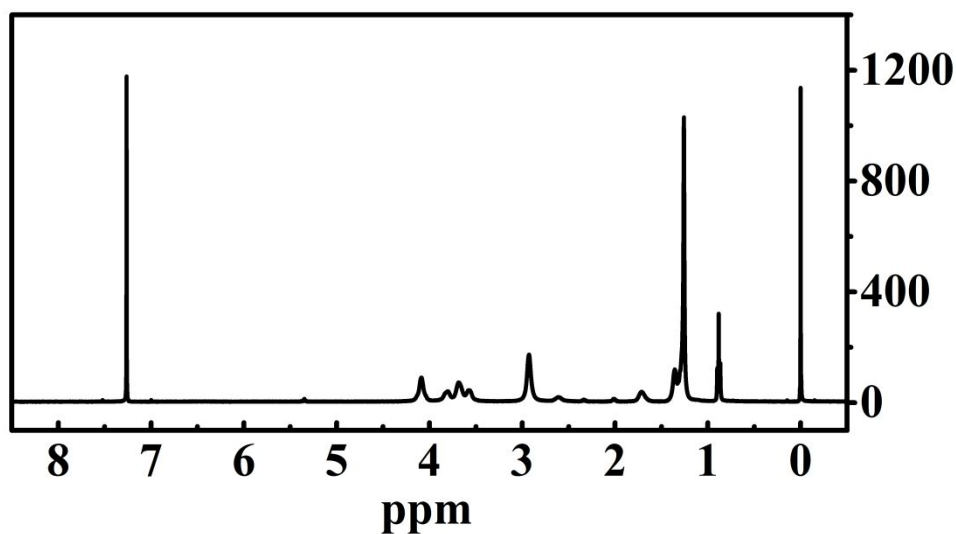


Figure S4. The  $^1\text{H}$  NMR spectra of PDHDB

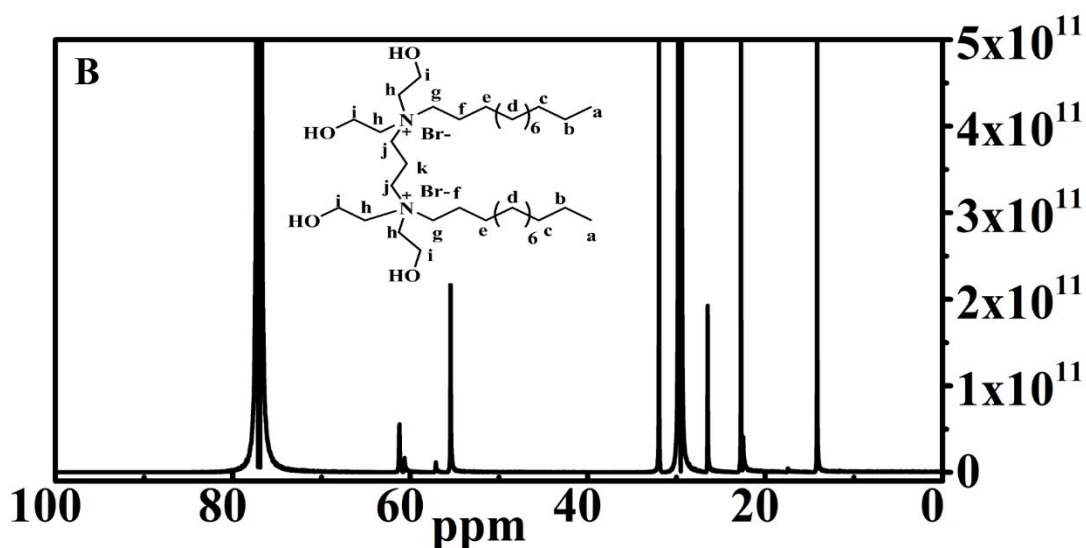


Figure S5. The  $^{13}\text{C}$  NMR spectra of PDHDB

The  $^1\text{H}$  NMR of PDDB (400 MHz,  $\text{CDCl}_3$ , TMS, ppm):  $\delta$  0.88 (t, 6H), 1.26 (s, 36H), 1.82 (s, 4H), 2.82 (s, 2H), 3.34 (s, 12H), 3.45 (s, 4H), 3.97 (s, 4H).

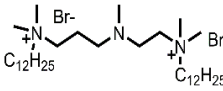
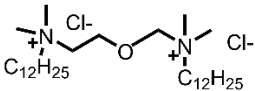
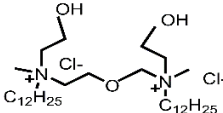
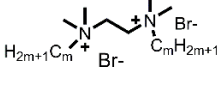
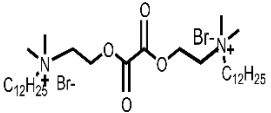
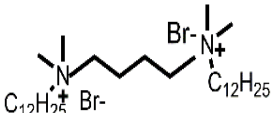
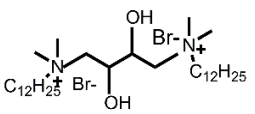
The  $^{13}\text{C}$  NMR of PDDB (150 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  14.12 C(a), 18.78 C(j), 22.68 C(b), 22.98 C(f), 26.35 C(e), 28.44 ~30.17C(d), 31.90 C(c), 51.29 C(h), 60.96 C(i), 66.46 C(g).

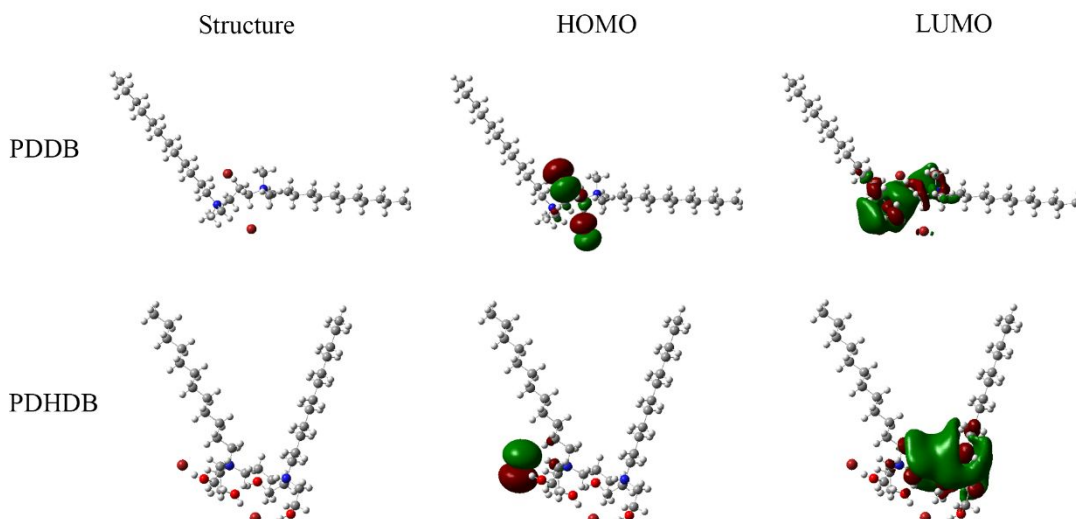
The  $^1\text{H}$  NMR of PDHDB (400 MHz,  $\text{CDCl}_3$ , TMS, ppm):  $\delta$  0.87 (t, 6H), 1.26 (s, 36), 1.71 (s, 4H), 2.61 (s, 2H), 3.45 ~3.96 (m, 16H), 4.09 (s, 8H).

The  $^{13}\text{C}$  NMR of PDHDB (150 MHz,  $\text{CDCl}_3$ , ppm): 14.13 C(a), 17.42 C(k), 22.39

C(b), 22.71 C(f), 26.47 C(e), 28.29 ~30.97 C(d), 31.96 C(c) , 55.45 C(j) , 57.08 C(g) ,  
60.64 C(h) , 61.20 C(i).

**Table S1. Comparison between various cationic surfactants as corrosion inhibitors of mild steel in acidic solution.**

Inhibitor	Concentration of Inhibition (/mol L <sup>-1</sup> )	Inhibition Efficiency (IE%)	note	References
<b>1</b> 	3N-12	1×10 <sup>-4</sup>	61	In 3 M HCl at room temperature. [3]
<b>2</b> 	12-O-12	1×10 <sup>-3</sup>	72	In 3 M HCl at room temperature. [4]
<b>3</b> 	12-MOH-O-MOH-12	1×10 <sup>-3</sup>	85	
<b>4</b> 	10-2-10	1×10 <sup>-5</sup>	76.3	In 1 M HCl at 303 K [5]
<b>5</b> m=10 , 12	12-2-12		83.2	
<b>6</b> 		1×10 <sup>-4</sup>	86.52	In 1 M HCl at 298 K [6]
<b>7</b> 	12-4-12	1×10 <sup>-5</sup>	78.2	In 1M HCl at room temperature with 1h [7]
<b>8</b> 	12-4(2OH)-12		82.5	



**Figure S6. Optimized geometric structures and frontier molecular orbital (HOMO and LUMO) for PDDB and PDHDB compounds.**

**Table S2. Quantum chemical parameters calculated using the Gaussian 09 program package with B3LYP/6-31G (d, p) basis set for PDDB and PDHDB compounds.**

	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\Delta E$ (eV)
PDDB	-4.8629	1.0576	5.9205
PDHDB	-4.5615	0.3771	4.9386

The Quantum chemical calculation was performed by the Gaussian 09W software. At the same time, the B3LYP functional with 6-31G (d, p) basis set was used to geometrically optimize the structures by density functional theory (DFT).

The optimized geometric structures, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) from Quantum chemical calculation were showed in Figure S6. The corresponding parameters, i.e., the energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), the the energy of the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ) and their energy gap ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ), were showed in Table S2.

The  $E_{\text{HOMO}}$  value is related to the electron donating ability of the compound. The

higher the  $E_{\text{HOMO}}$  value, the stronger the electron-donating ability, which suggests the inhibitor molecular donates electron more easily to the vacant orbital of the metal, thereby retarding the metal corrosion.<sup>8</sup> The order of  $E_{\text{HOMO}}$  follows PDDB < PDHDB, illustrating PDHDB could have a better inhibition effect than PDDB. This is consistent with our experiment results. On the other hand, the  $E_{\text{LUMO}}$  value indicates the electron accepting ability of one molecule. By contrast, the lower the  $E_{\text{LUMO}}$  value, the higher the ability of accepting electrons. Therefore, a decreasing  $E_{\text{LUMO}}$  suggests the better inhibition efficiency.<sup>9</sup> Also, the order of  $E_{\text{LUMO}}$  is PDDB > PDHDB in Table S2. Similarly, this trend is in agreement with the experimental data. The  $\Delta E$  value between  $E_{\text{LUMO}}$  and  $E_{\text{HOMO}}$  is another important factor in describing the molecular activity. When the  $\Delta E$  value decreases, the inhibitor efficiency is improved.<sup>10</sup> The trend for the  $\Delta E$  values follows the order PDDB > PDHDB, which suggests that PDHDB would adsorb on the metal more easily to prevent the metal from the corrosion effectively.

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