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Symmetry effect of cobalt phthalocyanines on the aluminium corrosion inhibition in hydrochloric acid

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ABSTRACT

The aluminium corrosion retardation potentials of phthalocyanine-based dyes, cobalt (II) 2,9,16-tris(4-(*tert*-butyl)phenoxy)-23-(pyridin-4-yloxy)phthalocyanine (**D1**) and cobalt (II) 2,9,16,24-tetrakis(4-(*tert*-butyl)phenoxy)phthalocyanine (**D2**) in 1 M hydrochloric acid were evaluated. Results from potentiodynamic polarization measurements show that inhibition efficiency increased with inhibitor concentration at 28 °C with values of 91.9 % and 87.0 % values respectively for **D1** and **D2** at 10 μM.

1. Introduction

Acid solutions have vital applications in industrial pickling and/or cleaning of metal surfaces such as aluminium [1,2]. This cleaning process attacks metal surfaces, deteriorating metal facilities and compromising services. Adding corrosion inhibitors cause corrosion processes of these important industrial activities to slow down. Organic corrosion inhibitors are effective, less costly and environmental friendly compared to their inorganic counter parts [3–7], hence are employed in this work. The presence of heteroatoms (N and O) enhance inhibition properties [8].

Phthalocyanines (Pc) are 18 π-electron aromatic macromolecules that possess four isoindole units linked by nitrogen atoms, prerequisites for corrosion retardation molecules. There are reports on Pc ligand system substituted with *tert*butyl derivatives [9], or containing cobalt central metal [8,10] for use in corrosion inhibition, but using symmetrically substituted Pc. This work presents an asymmetric cobalt (II) 2,9,16-tris(4-(*tert*-butyl)phenoxy)-23-(pyridin-4-yloxy)phthalocyanine (**D1**) and its symmetric counterpart cobalt (II) 2,9,16,24-tetrakis(4-(*tert*-butyl)phenoxy)phthalocyanine (**D2**), for the first time, as corrosion inhibitors in 1.0 M HCl solution. Symmetry reduction of Pcs has been found to improve the opto-electronic and electrochemical properties of these macrocycles [11]. Herein, enhanced corrosion inhibition is established at low concentrations for **D1** and **D2**, to guarantee ambient concentrations that can be naturally taken care of easily.

2. Experimental section

Equipment items may be found in the Supporting Information.

$Co(CH_3COO)_2$, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 1-pentanol, methanol (MeOH), ethanol (EtOH), chloroform ($CHCl_3$) were obtained from Sigma-Aldrich. 4-(4-Pyridyloxy) phthalonitrile and 4-*tert*-butylphenoxy phthalonitrile were earlier synthesized [12,13]. The synthesis of **D2** has been reported [14], but was obtained as a byproduct for **D1** synthesis hence reported in this work. 4-(4-Pyridyloxy)phthalonitrile (0.1 g, 0.45 mmol), 4-*tert*-butylphenoxy phthalonitrile (0.372 g, 1.35 mmol), $Co(CH_3COO)_2$ (0.08 g, 0.45 mmol) and a catalytic amount of DBU in dry 1-pentanol (3 mL) were mixed and heated at 160 °C with stirring under nitrogen for 24 h, cooled to room temperature followed by addition of methanol. The product was collected by centrifuging, washed severally with methanol and ethanol and dried in vacuo. The crude material was subjected to silica gel column chromatography and eluted with $CHCl_3$ with **D2** first eluted then **D1**, separately because of different solubilities.

Cobalt (II) 2,9,16-tris(4-(tert-butyl)phenoxy)-23-(pyridin-4-yloxy)phthalocyanine (**D1**) – Yield: 3% (15 mg). FT-IR (UATR-TWO^{TM}) ν max/cm^{-1}: 3066 (Ar-CH), 2955–2868 (Aliph., CH), 1599,1508 (C = C), 1463–1362 (C–C), 1235 (Asym C–O), 1045 (sym.C-O), 959, 823, 744 (C–H out of plane deformation). UV–Vis (DMSO) λ_{max} (nm): 607 (3.36), 668 (3.81), MALDI-TOF MS *m/z*: Calculated: 1109.17; found: m/z = 1111.13 $[M + 2H]^+$. Elemental analysis: Anal. Calc. for $C_{67}H_{55}CoN_9O_4$ (%): C, 72.55; H, 5.00; N, 11.37; found (%): C, 72.61; H, 4.95; N, 11.42.

Cobalt (II) 2,9,16,24-tetrakis(4-(tert-butyl)phenoxy)phthalocyanine (**D2**) – Yield: 7.6% (40 mg). FT-IR (UATR-TWO^{TM}) ν max/cm^{-1}:

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