A.C. and D.C. Voltammetry in Liquid Naphthalene Solutions: Stepwise Electrode Potentials for Metal Phthalocyanines and Porphyrins in Strictly Non-co-ordinating Media

Ross H. Campbell,[a] Graham A. Heath,*[a] Glenn T. Hefter,[b] and Roderick C. S. McQueen[a]

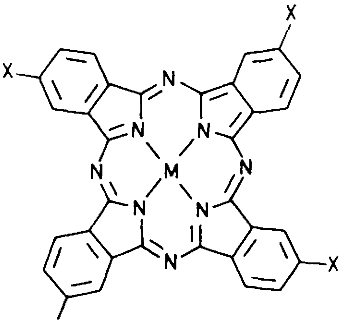
[a] *Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, Scotland*
[b] *School of Mathematical and Physical Sciences, Murdoch University, Western Australia, 6150, Australia*

Liquid naphthalenes prove to be convenient and versatile solvents for voltammetric measurements, and have revealed a very orderly relationship in electrode potentials for thirty phthalocyanines and porphyrins in non-co-ordinating media at 150 °C (423 K).

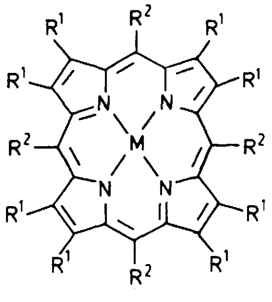
The insolubility ($<10^{-6}$ M) in common solvents of most metal phthalocyanines, [MPc], (**1a**), which has greatly restricted their study in the past, prompted us to undertake voltammetric studies in liquid naphthalene media at elevated temperatures. Although they would not normally be regarded as feasible solvents for electrochemistry, we find that 1-methylnaphthalene (MeNp) and 1-chloronaphthalene (ClNp), with dielectric constants 2.7 and 3.7 and b.p. 245 and 260 °C, respectively, provide convenient highly conducting media in the presence of 1 M $Bu^{n}_{4}NBF_4$, $Bu^{n}_{4}NClO_4$, or $Bu^{n}_{4}NPF_6$ at 150 °C (423 K). In such solutions, a.c. and d.c. polarography and stationary electrode voltammetry are readily achieved with conventional cells and commercially available instrumentation (Figure 1). Similar results are obtained in molten naphthalene itself.

Under these favourable conditions, the phthalocyanine pigments, though still generally $<10^{-5}$ M, show two distinctly resolved reversible one-electron reductions. The resulting $E_{\frac{1}{2}}$ values are listed in Table 1, together with those obtained for metal tetraphenylporphin [MTPP] and metal octaethylporphin [MOEP] systems (**2a**) and (**2b**) respectively, and likewise for organosoluble [M(PcBu$^{t}_{4}$)] complexes (**1b**) which we have prepared in the course of this work. After extensive cross-checking of selected mixtures we present these data as a self-consistent set of relative electrode potentials (within 10 mV) for the various free-base macrocycles and their important metalloderivatives, directly compared in strictly non-co-ordinating media.

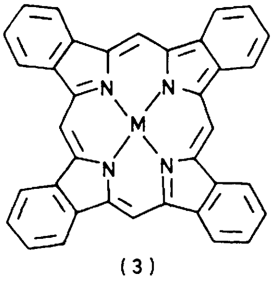
Reassuringly, there is a much closer resemblance in the pattern of reduction potentials for phthalocyanines and por-



(1) a; X = H
b; X = Bu^t
c; X = SO_3^-



(2) a; R^1=H, R^2=Ph
b; R^1=Et, R^2=H



(3)

Table 1. Electrode potentials ($E_{\frac{1}{2}}$/V) for phthalocyanines and porphyrins.

		E_{red} (1) and E_{red} (2) *vs. in situ* $[\text{Fe}(\text{C}_5\text{H}_5)_2]^{+/0}$ [a]						
Macrocycle	Medium[b]	(M =) H_2	Mg	Zn[c]	Cu	Ni	Co	Fe
(1a)[d]	MeNp/150 °C	−1.15 −1.60	−1.53 −2.0	−1.34 −1.70	−1.26 −1.70	−1.28 −1.76	−1.20 −1.90	−1.26 −1.69
(1b)	MeNp/150 °C	−1.17 −1.66	−1.60 —	−1.39 −1.77	−1.30 −1.74	−1.32 −1.80	−1.20 —	−1.41 −1.72
(1b)	CH_2Cl_2/20 °C	−1.17 −1.58	−1.60 —	−1.39 −1.74	−1.31 −1.71	−1.34 −1.76	−1.20 —	−1.40 −1.75
(1b)	Me_2SO/20 °C	−1.20	—	−1.46	−1.31	−1.35	−1.25	−1.62
(2a)	MeNp/150 °C	−1.59 −1.99	−1.89 —	−1.75 −2.16	−1.70 −2.15	−1.67 −2.22	−1.29 —	— —
(2b)	MeNp/150 °C	−1.78	—	−1.99	−1.91	−1.82	−1.44	−1.65

[a] A.c. polarographic values; apparent $E_{\frac{1}{2}}$ *vs.* saturated calomel electrode for $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ = *ca.* +0.56 (MeNp), +0.55 (CH_2Cl_2), and +0.50 V (Me_2SO). [b] Absorption spectra of hot MeNp solutions are *normal*, ruling out macrocyclic aggregation at 150 °C in the range 10^{-7} to 10^{-4} M. [c] In MeNp, E_{ox} (1) for **(1a,b)** and **(2a,b)** (M = Zn) = +0.22, +0.19, +0.40, and +0.28 V respectively. [d] For **(1a)** (M = Mn, Pt, and Pb) in MeNp, E_{red} (1) = −1.27, −1.23, −1.27 and E_{red} (2) = −1.72, −1.61, −1.57 V respectively.

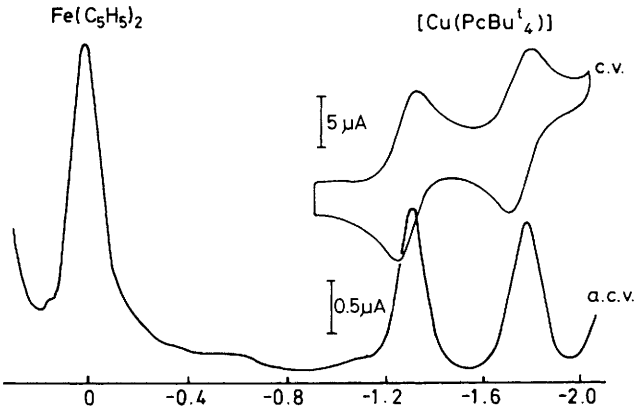


Figure 1. Voltammetry of copper tetrabutylphthalocyanine in 1-methylnaphthalene recorded *vs.* ferrocene in MeNp–$Bu^n_4NBF_4$ at 150 °C, with a molten $Ag/AgNO_3$ reference electrode and a polished Pt disk for cyclic voltammetry (c.v.) and an electronically timed dropping mercury electrode for a.c. polarography (a.c.v.), using a PAR 170 electrochemistry system with positive feed back resistance compensation and phase-sensitive a.c. detection at 205 Hz. Scan rates are 100 mV s^{-1} (c.v.) and 10 mV s^{-1} (a.c.v.), and the effective cell resistance, R_u, is typically 500 Ω.

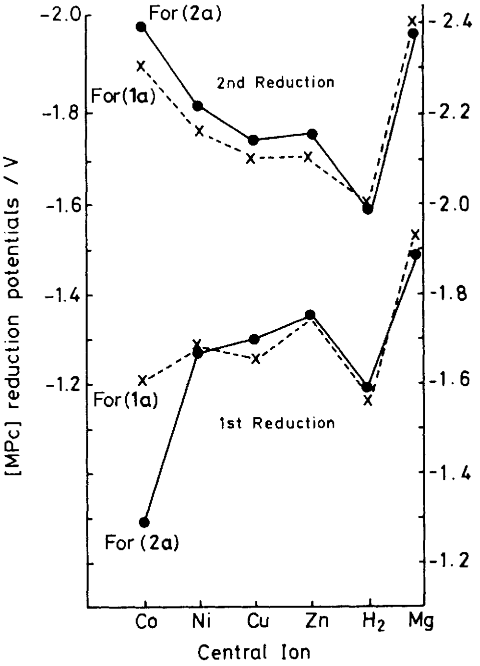


Figure 2. Trends in reduction potentials, using MeNp/150 °C values from Table 1; note the relative displacement of data sets by 0.40 V. **(1a)** = [MPc], **(2a)** = [MTPP].

phyrins than apparent hitherto.[1–6] Thus **(1)** and **(2)** have similar characteristic separations of $E_{\text{red}}(1)$ and $E_{\text{red}}(2)$ (reflecting stepwise electron addition to analogous doubly degenerate LUMO levels), and the interesting metal-dependence profiles typified by Figure 2 are broadly parallel.

For unambiguously ligand-based reductions where M = H_2, Mg, Zn, Cu, and Ni, we find virtually superimposable profiles for **(1a—c)** and likewise for **(2a,b)**. A distinct inversion between **(1)** and **(2)** is identified in the order of reduction of Cu^{2+} and Ni^{2+} complexes. Plots of the refined $E_{\text{red}}(1)$ data show only shallow and erratic correlations with central ion electronegativity (least squares correlation coefficient = 0.70 on the Allred–Rochov scale and 0.87 on the revised Pauling scale, for all appropriate [MPc]), of no predictive value among the transition metal derivatives. The case for such a dependence on electronegativity or any other exclusively metal-based parameter[6–9] has evidently been overstated.

Since the inclined *meso*-phenyl groups of [MTPP] have a negligible substituent effect,[1] Figure 2 directly quantifies the intrinsic difference in electron affinity of phthalocyanine and porphin ring systems (*ca.* 0.4 eV). Characterisation of the structurally intermediate zinc tetrabenzoporphin **(3)** reveals that tetra-aza bridging actually tends to lower the acceptor orbitals by 0.6 eV, while the fused benzene rings have a *destabilising* influencing of 0.2 eV. (This scarcely self-evident conclusion is accommodated by semi-empirical MO calculations.[10]) On the other hand, E_{red} (1) values for the Co^{II}/Co^{I} process of [CoPc] and [CoTPP] tend to converge. Thus, in distinction to previous reports,[1,2] the position of the cobalt complex *relative to other members* is markedly different in the phthalocyanine and porphyrin series.

The briefly reported observation of [MPc] oxidations by orthodox cyclic voltammetry in ClNp at 20 °C[11] conflicts with our experience. Indeed, soluble substituted phthalocyanines **(1b,c)** generally show only anomalous poorly-defined anodic response.[3,12] Fortunately both [ZnPc] and [Zn(PcBu$^t_4$)] give well-behaved one-electron oxidations in MeNp at 150 °C (and the latter likewise in 1,2-dichlorobenzene[12]). The measured separation between oxidation and reduction, $\Delta E_{\frac{1}{2}}$, does not match the energy of the prominent π–π^* visible absorption band (1.57 V *cf.* 1.82 eV), demonstrating that for phthalocyanines, unlike porphyrins, photo-excitation arises from an orbital below the HOMO.

We have also shown (Table 1) that no significant differences exist between high- and low-temperature $E_{\frac{1}{2}}$ data for such macrocycles in non-co-ordinating media and that, among redox-inert central ions, the zinc complexes are markedly the most sensitive to donor solvents. For example, in Me_2SO the ligand-based couples of $[Zn(PcBu^t_4)]$, and likewise [ZnOEP], are shifted by *ca.* −70 mV relative to other derivatives (M = Ni, Cu, and H_2) although $\Delta E_{\frac{1}{2}}$ is unchanged (and equal to its value in dimethylformamide[9]).

Besides their high-temperature operating range and unusual effectiveness as solvents, liquid naphthalene electrolyte media are notable for their non-polar, non-co-ordinating, aprotic (and strictly anhydrous) qualities, and they should find wider application in organic and inorganic electrochemistry.

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