Eclética Química

A model for specific interactions of manganese-phthalocyanine in protic media

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ABSTRACT: Extinction coefficients (e) changes of manganese phthalocyanine (Mn-Pc) were studied in different organic solvents and related to solvent polarity scales (Kosower's values (Z), Dimroth's values (E_T), donor numbers (DN) and linear solvation energy relationships (LSER) or linear free energy relationships (LFER)), theoretical molecular orbital calculations and ligand/solvent coordination processes in order to predict molecular interaction with the medium and identification of predominant intermolecular forces.

KEYWORDS: Manganese-phthalocyanine; solvent scales; U.V.-visible spectra; solute-solvent interactions; intermolecular forces.

Introduction

The considerable variations on molecular chemistry properties has long been known to be influenced by medium interaction. The electronic spectrum of a immersed molecule in a solvent generally suffers a shift in energy related to the spectrum of the isolated molecule in the gas phase at low pressure.[1,2,30] The solvent effects on solution reactivity is of fundamental importance in nearly all fields of chemistry. The increased interest in dipolar aprotic solvents due to high dieletric constant[11,24,27] in comparison to alcohol solutions, makes those systems particularly interesting for acid-base studies for a wide range of organic reactions. The more "chemical" properties include polarity, ability to form hydrogen bonds(HB), and structuredness. Linear free energy relationships (LFER) or linear solvation energy relationships (LSER) relate such properties to divers processes in solution, such as solubility, rates of reaction, wavelength of light absorption, and so on.[20] The solvation energy is defined as the energy change which accompanies the transfer from a molecule at the gas phase (or vacuum) to a liquid solvent.[28] Usually, most of the chemical processes are concerned with molecules in condensed phases, such as liquids and solutions.[31] The photophysical properties of liquids are determined by nature and energy of their electronically excited states.

Solvent effects on discrete low-energy spectra in the optical and ultra-violet (UV) energy regions, the so called solvatochromatic shifts, in particular the question of red versus blue absorption shifts following solvation of organic species with B electron system has been the subject of intensive investigation.[10, 27]

Classical solute-solvent interactions can be non-specific (dielectric interactions) when they depend on polarity properties of the solute and solvent molecules, arising from the Coulomb forces between charged ions or dipolar molecules and polarization forces from induced dipole moments in molecules due to nearby ions or dipolar molecules.[24] Specific solute-solvent association, with charge dispersion and formation of hydrogen bond between specific sites of the solute-solvent molecule, locked in a well defined geometrical situation,[24] occurs when solute-solvent of fixed stoichiometry and geometry are formed.[11,20,24] A specific association implies a fixed stoichiometry (usually 1:1), as well as fixed geometry (bond length and angle). Different scales that relate solubility properties such as Z, E_T and DN are expressed in kJ.mol^{-1} from 0 to 100 and are not comensurate[20] with normalized parameters ", a , b and p* that range from 0 to 1.

Symmetry perturbations due to ligands directed to the central metal is defined as axial ligation[6,7,11,18,29] which can be compared to the spatial arrangement in combination o geometric factors of the weaker solvent coordination processes. Spectral properties of phthalocyanines (Pc) act as an excellent guide to the accuracy of theoretical treatments for coordination of basic ligands and solvents with charge transfer processes between the metal and Pc ring[7,9,12,13,18] and deduction of the oxidation state of the central metal.

In this work the interaction of manganese-phthalocyanine (Mn-Pc), by considering changes on the molar extinction coefficient (e- M^{-1}.cm^{1}), are described. Solubility properties (e values) for Mn-Pc were related to solvent scales and compared to solvent/ligand coordination processes. The evidences for specific interactions have been interpreted as dependent from the inserted Mn (d and paramagnetic metal) on the phtalocyanine ring and related to the theoretical values obtained by calculation using the extended Hückel method (EHM).[26]

Experimental

Manganese phthalocyanine (Mn-Pc) was obtained from Eastman Kodak Co., Rochester, N. Y. U.V. - Visible absorption spectra was recorded on a Hewllet-Packard-8000 diode array and on a Bausch and Lomb-mod. spectronic 2000 spectrophotometer.

All solvents and chemicals were of analytical grade. Benzene was distilled over sodium. Water was double-distilled and deionized. Spectral measurements were carried out under conditions without aggregation of the solute molecules. The Lambert-Beer law was fulfilled in all solvents, so that solvent-induced band shifts or solubility changes were not due to association phenomena (see Figures 1-4). Under the assumptions of Debye-Hückel theory, no correction is necessary for reference to infinitely dilute solutions, because phthalocyanine (Pc) concentrations were measured in the concentration range of 10^{-7}M (M = mol.dm^{-3}).
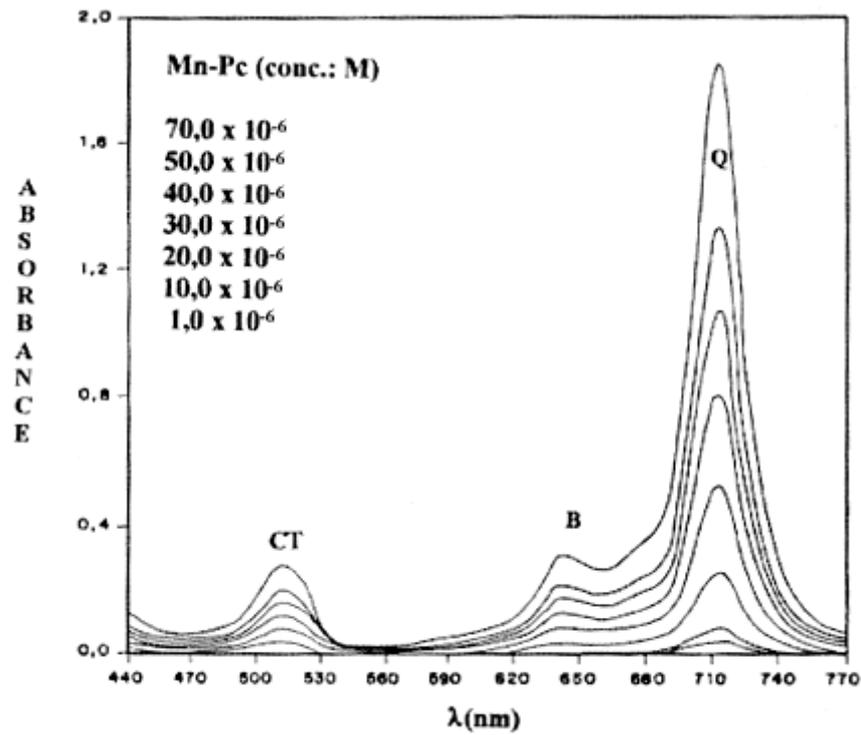
FIGURE 1 - Absorption spectra of Mn-Pc in ethanol at 298.15 K.
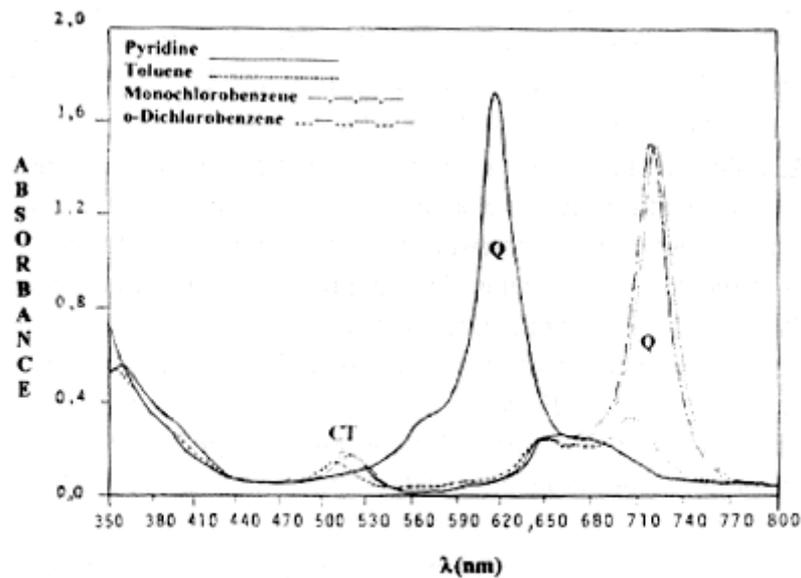
FIGURE 2 - Absorption spectra of Mn-Pc in pyridine (conc.:0.34 x 10^{-4}M);
toluene (2.00 x 10^{-4}M); monochlorobenzene (2.50 x 10^{-4}M) and
odichlorobenzene (0.20 x 10^{-4}M), respectively at 298.15 K.
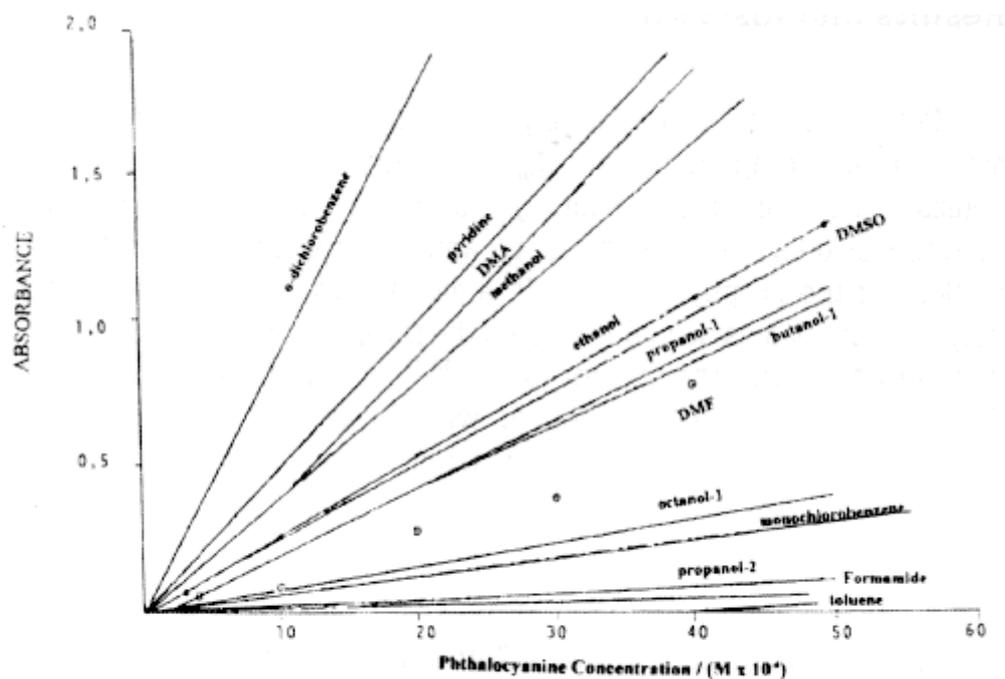
FIGURE 3 - Representation of the absorption data (Beer-Lambert curves) for Mn-Pc in different solvents at 298 K.
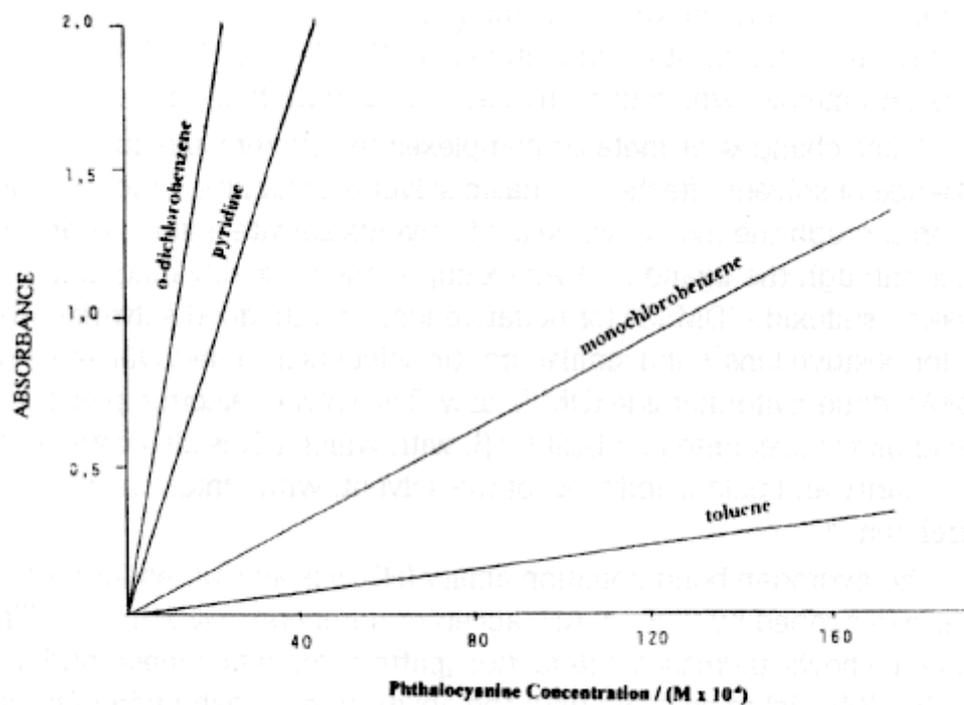
FIGURE 4 - Representation of the absorption data (Beer-Lambert curves) for Mn-Pc in different solvents at 298 K.

Dymethylformamide (DMF) hydrolyses at relatively fast rate in the presence of acids or bases.[37] A few concentration points deviated from Beer-Lambert Law for Mn-Pc in DMF due to the mentioned

effect ([Figure 3](#)).

Results and Discussion

Phthalocyanine is a relatively small planar molecule containing 56 atoms in an arrangement with D_{4h} symmetry. The closed inner system consists of 16 carbon and 8 nitrogen atoms (18 p electrons, corresponding to Hückel's rule for aromaticity) has great stability, forming the nucleus of the porphyrins.[7,9,18] It is also known that the metal atoms may be more or less delocalized from the molecular plane, depending on its interaction with the solvent media.[14,35,36] The B electron system of the phthalocyanato ligand interacts with the central atom and, depending on its electronegativity, conferes donor or acceptor character to the molecule.[15,22,29]

Manganese-phthalocyanine - Solvent Interactions Correlated among Solvent Polarity Scales

Low solubility of metallo-phthalocyanines (M-Pc) has lead to the situation where spectral data are presented mostly in the same solvents for ranges of phthalocyanine compounds. In addition, e, values are roughly taken in almost all laboratories as 10^5 M^{-1}.cm^{-1} for different solvents and metals, which in many cases is far from being real.

Collor changes of metallic-complexes in different medium are an evidence of solvent effects[15,22]. Basic solvents solubilizes cations (s-donation through the metal), while acid solvents solvates anions (s-acceptance through the ligand)[3,28]. As example, the poor solvating ability of dimethyl sulfoxide (DMSO) for negative ions and its good solvating ability for positive ions[12] and similar aprotic solvents as dimethyl acetamide (DMA), dimethyl formamide (DMF), asw. The solvent electron pair donation ability is accounted for best by b , with which D.N. is also correlated; the polarity and polarizability p* of the solvent , with which the basity is correlated.[24]

The hydrogen bond donation ability (HBD) is accounted for best by a , also described by Z, E$_T$,[30] A.N. (acceptor numbers) and acity.[24,27] The [Table 1](#) shows increased interaction pattern for manganese-phthalocyanine (Mn-Pc) in solvents with the ability to establish hydrogen bindings, once its solubilization increases with the donicity of protic solvents (Gutmann DN, Z and ET scale, and a ; a measures the hydrogen-bond donor ability of the bulk solvent, related by a multiparameter equation, called linear solvation energy relationship (LSER)[11,20,24]) and decreases with the donicity of aprotic solvents. The absence of a solubilization pattern in dipolar aprotic solvents shows that dielectric/polarity effects are not the primary intermolecular forces contributing to Mn-Pc solubilization processes. The strongest hydrogen bonds (HB) are expected to occur between a solvent (protic) with its conjugated base;[25,32] in this case, the outer-bridged nitrogen atoms of the Pc ring. According to calculations,[26] Mn in an phthalocyanine(Pc) environment, presents atomic charge and ligand population respectively, +0.101 and -0.101. The low permanent molecular dipole moment, induces hydrogen binding with increased solubility pattern for the alcohol hydrogen bond donation ability (a)[20,24] so that it can be classified an acidic indicator for organic solvents. Those assumptions are confirmed by its distinct solubility pattern in aromatic solvents ([Table 2](#)). Mn-Pc presents no regular pattern for polarizability/dipolarity interactions; but with the register of charge

dispersion and formation of hydrogen bonds, ability of protic solvents.

Table 1 - Values of λ_{max} for the Q-band of manganese-phthalocyanine and solvent scale values (298,15 K)

Molecule	Organic Solvents	λ_{max} (nm) (t.w.)	Z scale (kJ.mol⁻¹) (ref. 6 and 7)	E_t scale (kJ.mol⁻¹) (ref. 6 and 7)	$DN_{Gutmann}$ (kJ.mol⁻¹) (ref. 6 and 7)	$DN_{calc.}$ (kJ.mol⁻¹) (ref. 6 and 7)
Mn-Pc	Pyridine	618	15,30	9,61	7,91	7,70
	DMA	705	15,99	10,44	6,64	6,88
	DMF	706	16,37	10,47	6,35	6,62
	Propanol-2	715	18,24	11,62	-	-
	Methanol	716	19,98	13,26	4,54	7,77
	Ethanol	716	19,02	12,40	-	7,38
	Propanol-1	717	18,71	12,12	-	-
	Butanol-1	717	18,57	12,00	-	7,00
	DMSO	717	16,78	10,75	7,12	7,19
	Mono-chlorobenzene	719	13,86	8,96	-	0,62

t.w. = this work

Table 2 - Solubility or absorption coefficient (ε) values for Mn-Pc in protic and aprotic solvents and its correlation with solvent polarity scales at 298.15 K

	Organic Solvents	λ_{max} – Q_{band} log ε		Z_{scale} (kJmol^{-1}) (ref. 6 and 7)	$E_{t\ scale}$ (kJmol^{-1}) (ref. 6 and 7)	(D.N.) (kJmol^{-1}) (ref. 6 and 7)	LSER (ref. 8)
		t.w.	liter.				
	Toluene	3.53	-	-	8,10	0,84	0.00
	Formamide	3.55	-	19,9	13,53	9,54	0.71
Aprotic	Monochloro-benzene	3.67	-	-	12,93	-	0.62
	DMSO	4.39	-	16,78	10,76	7,19	0.00
Dipolar	DMF	4.45	-	16,37	10,47	6,62	0.00
	DMA	4.62	3.28[16]	15,99	10,44	6,88	0.00
Solvents	Pyridine	4.69	-	15,30	9,61	7,70	0.00
	o-Dichloro-benzene	4.94	-	14,34	-	0,19	0.00

⇓

Increase of ε (M^{-1}.Cm^{-1}) / Increase of Solubility

⇑

	Organic Solvents	λ_{max} – Q_{band} log ε		Z_{scale} (kJmol^{-1}) (ref. 6 and 7)	$E_{t\ scale}$ (kJmol^{-1}) (ref. 6 and 7)	(D.N.) (kJmol^{-1}) (ref. 6 and 7)	LSER (ref. 8)
		t.w.	liter.				
	Methanol	4.60	-	19,98	13,26	7,77	0.98
	Ethanol	4.43	-	19,02	12,40	7,39	0.86
Protic	n-Propanol	4.34	-	18,71	12,12	-	0.84
	n-Butanol	4.33	-	18,57	12,00	7,00	0.84
Solvents	n-Octanol	3.90	-	-	-	-	0.77
	2-Propanol	3.60	-	18,24	11,62	6,26	0.76

t.w. = this work
liter. = values cited in the literature
LSER = hydrogen bond donation ability of the solvent: see reference (8).

Axial Coordination of Solvents and/or Basic Ligands to Manganese-Phthalocyanine

The phthalocyanine ring itself can be symmetric. Perturbations to the geometry from D^{4h} to C$_{4v}$ of the central metal due to axial ligands or solvents, and the size effects of different central metals have been subject of intensive investigation.[9, 12, 13, 26] Previous studies[10,17,22] assign the Q band as an p (a$_{1u}$) ® p*(eg) transition and the B band as vibronically allowed, which gets intensity mainly in dimerization processes.[35]

The band around 500 nm is characterized as charge transfer transition[7,9,18,19,26] from metal to ligand [MLCT: d(e$_g$) ® e$_g$(p*); d(e$_g$) ® b$_{1u}$(p*)] or from ligand to metal LMCT: a$_{1u}$(p) ® d(e$_g$); a$_{2u}$(p)® d(e$_g$); a$_{2u}$(p) ® d$_z^2$(a$_{1g}$) (Figure 1). For axial ligand studies, the weakly coordinating

solvents DMA, DMSO and DMF provide a consistent environment from which to compare different metals and different axial ligands.[6] The coordination of Pc sites determines in part molecular behavior and spectral properties.[9]

Electron density can be transferred by p-back-donation from the metal in strong antibonding orbitals of the ligand,[19] so that changes in the M-N bond can be detected. When basic ligands(L) such as PY coordinates to the central transition metals of macrocyclic molecular solids, the axial ligation is accompanied with an angle shift of the long molecular axis in relation to the substrate, so that axially ligated molecules are more tilted-up; for Co-Pc complexes in Langmuir-Blodgett films the formed angle is 40° ; the L (PY) inclusion generates an angle shift to 60° . If a parallel can be drawn for transition metals,[5] the angle shift superimposes adjacent molecular units, enhancing orderliness and suppressing partially the additional intramolecular "connection" (cooperativity) between adjacent metal and nitrogen atoms. Removal of PY coordinated ligands to Mn-Pc showed enhanced crystalline disorder.[34] In pyridine(PY), Mn-Pc molecules are six-coordinated, with the PY molecules ligated axially and externally in the sixth coordination position,[6] the structure being bridged by an oxygen atom forming a bridged oxygen dimer: PY.Pc-Mn-O-Mn-Pc.PY. The PY coordination to the manganese atom is accompanied with a raise in energy of the dz^2 orbitals which is dependent on the degree of the axial perturbation. Since the ground state is S = 3/2 the spin change is accompanied with the triplet-multiplet states mixing,[4,5,17,31] once ^{3}(p ® p*) S = 1 can present overall spin 3/2 and mix with ^{1}(B6B*) S = 3/2 . Thus triplet-multiplet states are possible and related to spin conversion processes with pronounced spectral changes, such as demonstrated for MnPc/PY (see Table-1, l_{max}-Q-band: 618 nm). The broadening of the Q-band in pyridine suggest that there may be a mixture of species present.[7,14,18,35,36] In DMA and DMF solutions Mn(II) is considered high spin.[19]

Solvent p-donor/acceptor capability toward the planar B-system of the Pc molecule, can be designed. Analysis of the B band (normally located at 640 nm), shows constant values for Mn-Pc in alcohols (l = 642 nm), but delocalized for aromatic solvents as pyridine and toluene (l = 665 nm, Figure 2 and 4) and shift to lower energy attributed to the interaction of the p electron system of the solvent with the phthalocyanine ring, favoring p-back-donation.

Dimeric species can be formed due to direct linkages that place the Pc ring close enough in space, so that intramolecular association can occur.[29] Zinc phthalocyanine (Zn-Pc) in alcohol-based solvents, presents dimerization processes,[6] which is not the case for the repported data. For the solvents under investigation dimerization processes were detected solely for Mn-Pc in toluene (Figure 2), where the vibronicallly allowed B band at 620 nm gets intensity, as a result of excitonic coupling between the two p systems.[6,29]

The band shifts observed for Mn-Pc in both protic and aprotic media can be related to charge transfer (CT) processes,[29] lying in the same energy region as the B and Q bands. When CT and p-p* transitions overlap, a blue or red-shifted Q-band is observed.[35] Hydrogen bonding can present considerable solvatochromic effects.[11,20,24] Mn-Pc in alcohols present a general tendency for red-shiftted spectra (Q band-l_{max} = 717 nm; DMA: 705 nm, DMF: 706 nm), which may be related to

the higher dipole moment of the excited state, larger in alcohols[11,20] due to the stabilization of p*(Pc) orbital in the presence of a nearby protic solvent. Mn-Pc for all alcohol solutions ([Figure 1](), [Table 1]() and [2]()) present typical spectra of unaggregated or monomeric Pc species, demonstrating that specific interactions through hydrogen bindings from the alcohol extremity to the Pc ligand, with fixed stoichiometry are formed.

Precedent work[4] repports Mn-Pc as almost perfectly square planar molecule in he solid state. Mn-phthalocyanato d[5] presents a M-N distance[16] of 1.938 Å. Barraclough at all reported the metal-nitrogen angle path as approximatly 90° . The planar molecules are stacked in the lattice so that they occur at intervals of 4.7 Å, along the short monoclinic axis of the crystal and inclined at an angle of 45° . The stacking arrangement of the molecules in the lattice is such that two nitrogen atoms of each molecule lie exactly above and below Mn atoms to the nearest neighbors with a distance of 3.4 Å[4,5,16,25,32] ([Figure 5 (a)]()). In the solid state, the N atoms from one Pc molecule present axial location in relation to the Mn atom from the neighbouring Pc molecule, providing a pathway for electronic and magnetic superexchange interactions driven by intramolecular contacts, weaker in a liquid medium but not significantly altered in an protic environment. Proposed structure for alcohol-to-Mn-Pc coordination is in ([Figure 5(b)]()). In the liquid state cooperativity effects are low due to small orbital overlap;[17] total cooperativity is achieved in perfect crystals. Considering that solid and solution spectra of Mn-Pc are similar, a qualitative parallel is suggested for solid and solution molecular arrangement, by considering that in solution intermolecular contacts (M-N) of Mn-Pc are considerably reduced, but maintaining the same parallel structure as described for solid systems. The solubilization process for the phthalocyaninato macrocycle which poseses large p-electron system is suitable for the registration of specific intermolecular interactions. A hydrogen bond (271 mm[8]) connects the alcohol molecules to the negatively charged molecular moiety of the Pc ligand the outer-bridged nitrogen atom (N····H-O-R) suitable to localized charges due to solvent interactions.[28]
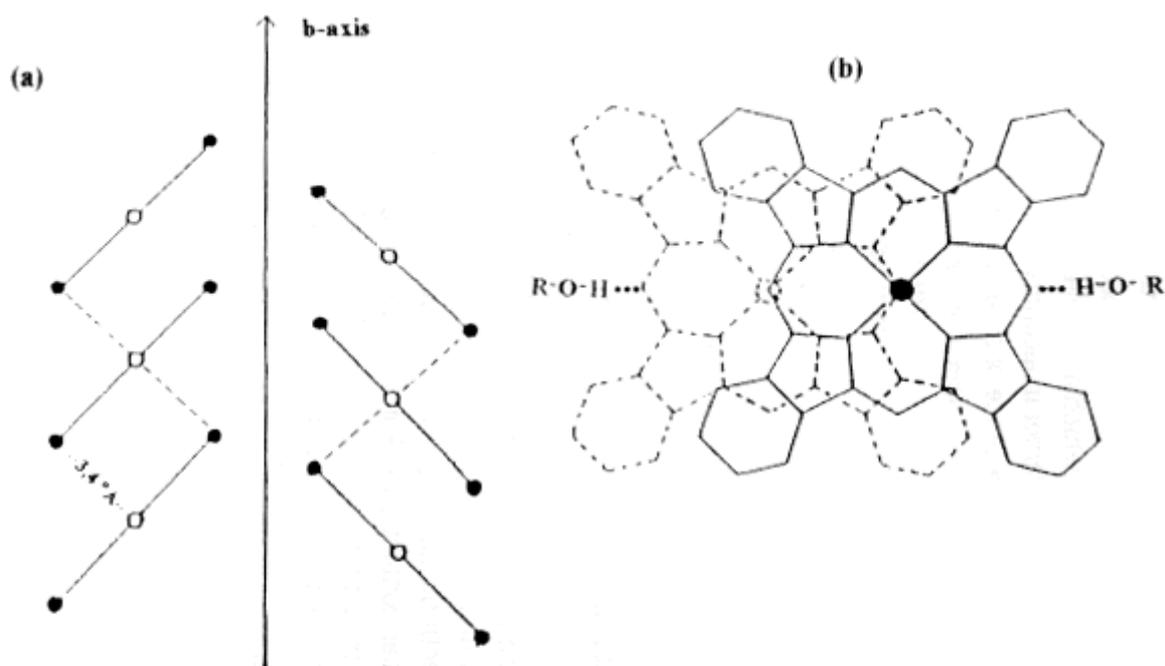
FIGURE 5 - (a) Stacking of Mn-Pc molecules along the b-axis; : Mn atoms; : N atoms, refs. 4,5. Two nitrpgen (N) atoms of each neighbouring molecule lie exactly above and below Mn atoms providing interactions (......) driven by intramolecular contacts (solutesolute interactions), (b) Normal projection of two parallel molecules of Mn-Pc wirh a residual cooperative intramolecular interaction (solutesolute: Mn-Pc-Mc-Pc) and intermolecular interactions (solute (MnPc)-solvent(R-OH) interactions) classified as specific interactions of hydrogen bondings type: a model for solubilization processes of Mn-Pc in alcohol (R-OH).

The additional intramolecular (MnPc-MnPc) binding between the metal and adjacent nitrogens remains as in the solid state, but weaker when solubilized in liquid media (alcohol solution) and needs to be accounted to deduce the structural disposition of Mn-Pc with respect to the neighbouring Mn-Pc molecule in the R-OH solution; the intermolecular forces responsible for solubilization processes are in proportion 1(solute-MnPc):1(solvent-alcohol) characterized as hydrogen bonding.

Conclusion

Manganese-phthalocyanine (Mn-Pc) was studied in different organic solvents. By considering its solvent interaction, due to its increased solubility pattern with the hydrogen bond donation ability of protic solvents, is an indication that dielectric/polarity effects are not the main contributing factors to Mn-Pc solubilization processes. A parallel between solid and solution spectra demonstrates qualitatively that a solvent(alcohol)-to-defined sites of the Pc ring, directed toward to the outer-bridged nitrogen atoms is formed in a fixed stoichiometry (1:1) and geometry (bond lenght and angle) providing pairwise intermolecular interactions and classified as specific interactions of hydrogen bondings type.

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RESUMO: Variações do coeficiente de extinção (e) para a ftalocianina de manganês (Mn-Pc) em diferentes solventes orgânicos foram correlacionados a escalas de polaridade, tais como, valores de Kosower (Z), valores de Dimroth (E_T), números doadores (DN) e relações lineares para energias de solvatação(LSER) ou relações lineares para energia livre (LFER), cálculo de orbitais moleculares e processos de coordenação ligante/solvente, objetivando o estudo da interação molecular com o meio e a identificação das forças intermoleculares predominantes.

PALAVRAS-CHAVE: Ftalocianina de manganês; escalas para solventes; espectros no U.V.-visível; interações soluto-solvente; forças intermoleculares.

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