

INTERACTION OF MAGNESIUM PHTHALOCYANINE WITH ORGANIC SOLVENTS

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Abstract. Magnesium phthalocyanine (Mg-Pc) is insoluble in water, but was solubilized in about fifteen different organic solvents at 25° C. In general, the interactions of Mg-Pc with solvents are of an electrostatic nature and occur preferentially with aprotic solvents that do not exhibit hydrogen bonding. This is explained by the s-electrons present in magnesium. Considering the interactions with the solvents, Mg-Pc may be classified as a basic indicator.

As part of a comprehensive study of the interaction of biological pigments with surfactants, micelles and membrane models¹⁻⁸ we have also investigated the solubilization of different phthalocyanines in aqueous solutions containing surface active agents and in various organic solvents. The present communication deals with some recent results that we have obtained for magnesium phthalocyanine (Mg-Pc).

Phthalocyanines are a class of organic compounds generally encountered in the leaves of plants that have an important role in the capture and transfer of energy. Besides, metal-phthalocyanine complexes are used commercially as dyes and pigments and have very interesting electrical, optical^{9,10} and spectroscopic properties.^{11,12}

Solubility data for phthalocyanines are rather scant in the literature. Mg-Pc is insoluble in water. We were able to solubilize it at 25° C in various organic solvents including dimethyl sulfoxide (DMSO); N,N-dimethylformamide (DMF), N-methylformamide (MF), formamide (F), pyridine, monochlorobenzene, o-dichlorobenzene, toluene, methanol, ethanol, n-propanol, isopropanol, n-butanol, n-octanol and others.

The spectrum at 25° C was determined in each solvent in the 350-800 nm region using a Bausch & Lomb Model Spectronic 2000 spectrophotometer. The solutions were prepared by stand-

ard gravimetric and volumetric methods and usually included ten to fifteen different concentrations of the pigment.

Figure 1 illustrates a typical absorption spectrum obtained for solutions of Mg-Pc in N,N-dimethylformamide (DMF) at 25° C. The more intense α -band occurs at 669±1 nm and

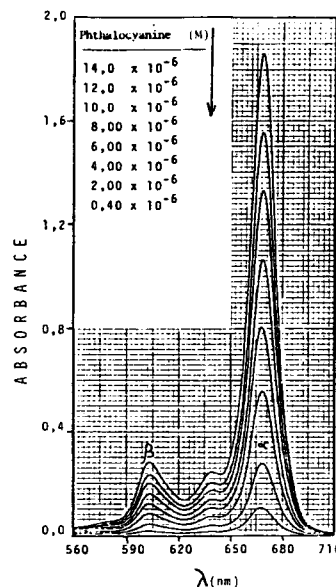


FIGURE 1. ABSORPTION SPECTRUM OF MAGNESIUM PHTHALOCYANINE IN N,N-DIMETHYLFORMAMIDE AT 25°C.

exhibits a shoulder at 639 nm. The α -band is generally attributed to $n \rightarrow \pi^*$ and metal-ligand ($M \rightarrow L$) or $L \rightarrow M$ transitions. The less intense β -band, attributed to $\pi \rightarrow \pi^*$ transitions occurs at 602 nm. The d-d band, present in metal-phthalocyanines containing d-electrons does not appear since Mg is a 3s metal.

In general, the wavelength of maximum absorption ($\lambda_{\max}$) of the α -band is affected by the solvent and exhibits a shift to higher wavelength in basic solvents. For example, in pyridine its value is 673 nm. The $\lambda_{\max}$ of the β -band changes little in most non-aromatic solvents. However, it exhibits shifts to higher wavelength (612 nm) in the presence of all aromatic solvents studied. This shift may be explained by interactions between the π -electron system of the solvent and that of the phthalocyanine ring.

Figure 2 illustrates Beer's Law plots for Mg-Pc in various organic solvents at 25°C. As can be seen, all the solvents exhibit linearity and do not show deviations in the 0-2 absorbance range. Mg-Pc is soluble in both protic and aprotic solvents. Excluding the results obtained for chlorobenzene and toluene, it can be concluded that in general Mg-Pc is more soluble in the group of aprotic solvents than in the group of protic solvents.

Some experimental extinction coefficient or molar absorptivity values ($\log a$) are as follows: isopropanol (5.31), DMSO (5.22), *n*-butanol (5.15), DMA (5.14), DMF (5.11), pyridine (5.10), *n*-octanol (5.06), *o*-dichlorobenzene (4.93), *n*-propanol (4.81), ethanol (4.58) and methanol (2.72).

Consideration of the experimental results obtained for Mg-Pc, the various classifications proposed for organic solvents in the literature^{13,14} in terms of dipole moment (μ), dielectric constant (ϵ), electrostatic factor ($EF = \mu \times \epsilon$), hydrogen bonding, protic and aprotic character, acidity and basicity and comparisons to Mn-Pc^{7,8} leads to the analysis summarized in Table I.

TABLE I. ANALYSIS OF THE SOLUBILITY AND INTER-ACTIONS OF MAGNESIUM PHTHALOCYANINE IN PROTIC AND APROTIC DIPOLAR SOLVENTS

Electrostatic Factor (EF)		Dielectric Constant (ϵ)	
Aprotic Dipolar Solvents	209	DMSO	46.6
	143	DMA	37.8
	140	DMF	36.7
	27.2	PYRIDINE	12.3
	24.9	ORTHODICHLOROBENZENE	9.9
	9.3	MONOCHLOROBENZENE	5.7
	0.9	TOLUENE	2.5
Decreasing Electrostatic - Decreasing Solubility Interactions			
Protic Solvents	54.1	METHANOL	32.6
	369	FORMAMIDE	109
	-	N-METHYLFORMAMIDE	-60
	40.8	ETHANOL	24.3
	33.3	<i>n</i> -PROPANOL	20.1
	-	<i>n</i> -OCTANOL	10.3
	29.9	<i>n</i> -BUTANOL	17.8
	30.7	ISOPROPANOL	18.3

As can be seen, the aprotic dipolar solvents follow a solubility order and distribution in accordance to that shown in Figure 2, while the protic solvents exhibit exactly the opposite order. The electrostatic factor (EF) follows the same pattern for aprotic solvents. For the protic solvents, its pattern is irregular, but the magnitude

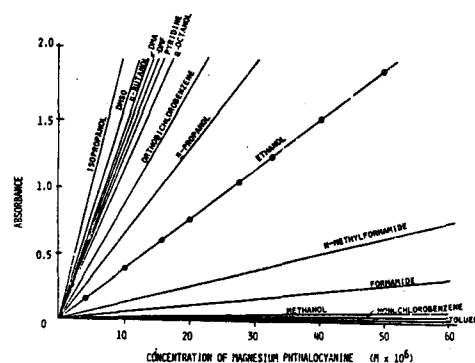


FIGURE 2. BEER'S LAW PLOTS FOR MAGNESIUM PHTHALOCYANINE IN VARIOUS SOLVENTS AT 25°C.

suggests that electrostatic interactions are important. These observations are also in general agreement with concepts of acidity and basicity described in terms of solvent donor (DN) and acceptor numbers (AN).^{15,16} Donor numbers for some of the solvents studied are as follows: pyridine (33), DMSO (30), DMA (28), DMF (27), formamide (24), ethanol (6) and chlorobenzene (-2).

Solubilization studies in aqueous solutions containing cationic, anionic, zwitterionic and simply polar surfactants can lead to correlation between the media of solubilization.^{7,8} For example, the spectrum of Mg-Pc in aqueous solutions with micelles of cetyldimethylethylammonium bromide is similar to that of Mg-Pc in *n*-octanol, suggesting that the environment in the two cases may be similar. On the other hand, the spectra of Mg-Pc in aqueous solutions containing micelles of Triton X-100 and BRIJ-35 that are polyethers are similar to those obtained in short-chain alcohols.

We suggest that magnesium phthalocyanine (Mg-Pc) may be considered as a basic indicator for solvent systems. Its interactions with solvents are more of an electrostatic nature, occur through coordination with Mg by σ -donation and are different from those observed for Mn-Pc.^{7,8}

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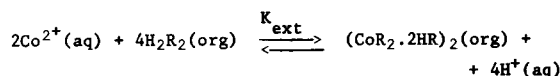
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EFFECT OF TEMPERATURE ON THE EXTRACTION OF Co(II) BY LAURIC ACID-PART V

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Abstract - The effects of the temperature on the extraction of Co(II) $1.06 \cdot 10^{-3}$ mol/L by Lauric acid 0.53 mol/L has been studied in the temperature range 293-323 K. The temperature dependence of the conditional constant of extraction is given in the form: $\ln K_{\text{ext}} = 12.80 - 4000.00 (1/T)$ with ΔH_{ext}^0 equal to 33.24 KJ/mol (endothermic process).

O estudo da extração de Co(II), em força iônica $1,0 \text{ mol/L}(\text{NaNO}_3)$, pelo ácido ricinolêico em tolueno, a 25°C , foi recentemente investigado¹ em função do pH da solução aquosa, como também em função das concentrações deste cátion e do ácido graxo. Verificou-se que o ácido láurico possui o mesmo poder de extração do ácido ricinolêico², e segue o mesmo esquema de extração seguinte:



onde $\text{H}_2\text{R}_2(\text{org})$ representa o dímero do ácido graxo (ricinolêico ou láurico) em tolueno e $(\text{CoR}_2 \cdot 2\text{HR})_2(\text{org})$ o dímero com 2 moléculas de solvatação por átomo de Co(II) extraído.

Nesta comunicação descreve-se o estudo do efeito da temperatura sobre a extração de Co(II) $1,06 \cdot 10^{-3}$ mol/L, em força iônica $0,5 \text{ mol/L}$, pelo ácido láurico (ácido n-dodecanóico) $0,53 \text{ mol/L}$ dissolvido em tolueno, no intervalo de temperaturas de 293-323K, em função do pH da fase aquosa.

O ácido láurico utilizado (reagente técnico de pureza de 98% da AGF-Ácidos Graxos Fracionados Ltda.) apresentou uma massa molar média de $201,02 \text{ g/mol}$; sua solução foi preparada em tolueno e padronizada com KOH alcoólico.

A solução aquosa de Co(II) foi preparada a partir de $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (p.a. da Merck), sua força iônica ajustada para $0,5 \text{ mol/L}$ com NaNO_3 (p.a., Merck) e padronizada com solução do sal dissódico de EDTA (p.a., Merck) em pH igual a 10 (tampão amônio-cloreto de amônio) utilizando-se murexida como indicador³.

Todos os demais reagentes utilizados neste trabalho foram de grau analítico.

As extrações de Co(II) pelo ácido láurico em tolueno foram realizadas pela agitação, durante 30 minutos, de 15 mL da solução aquosa deste cátion metálico com igual volume do ácido graxo em tolueno. Estas extrações foram realizadas em uma cela de vidro com camisa conectada a um banho termostático (Veb ML W Prufferate-Werb Medingen Sitz Freital, modelo U2 C) e este por sua vez ligado a um banho com circulação de água fria (Neslab Instruments, modelo Coolflow-33). Após este tempo, separou-se as duas fases em um funil de separação, mediu-se o pH da fase aquosa e a concentração de cobalto(II) não extraído desta fase foi determinada por espectrofotometria de absorção atômica no comprimento de onda igual a $240,7 \text{ nm}$ (Perkin-Elmer, modelo 305). Subtraindo-se este valor de concentração do valor da concentração inicial de Co(II), encontrou-se o valor da concentração de Co(II) extraído na fase orgânica e então o valor de D (razão de distribuição) foi calculado.

A Figura 1 mostra o comportamento de $\log D$ em função do pH da solução aquosa (região linear) para a extração de Co(II) $1,06 \cdot 10^{-3} \text{ mol/L}$ por ácido láurico $0,53 \text{ mol/L}$ nas temperaturas de 293,303,313 e 323K. Pode-se observar que em valores de pH maiores do que 6,8, a percentagem de extração obtida foi maior ou igual a 99% (extração em um ciclo), para as quatro temperaturas estudadas.