SOLVENT EFFECTS ON THE ELECTRONIC TRANSITION ENERGIES OF PORPHYRINS IN BINARY SOLVENT MIXTURES

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ABSTRACT. The UV-Visible absorption spectra of free-base and nickel porphyrins have been investigated in binary mixtures of solvents with similar polarities and dissimilar refractive indices. The Soret band energies of five porphyrins show significant correlations ($|r| = 0.98$ to > 0.99) with respect to the Lorentz-Lorenz function of the refractive index of the solvent mixture for ethyl acetate – chlorobenzene and ether – anisole mixtures. These correlations indicate a specific dependence of the porphyrin $\pi* \leftarrow \pi$ transition energies on the solvent polarizability, in contrast to the conclusions from a study using solvents across different classes (O.W. Kolling, *J. Phys. Chem.* 1989, 93:3436), and in agreement with the conclusions of a study using *n*-alkanes (I. Renge, *J. Phys. Chem.* 1993, 97:6582).

Keywords: Porphyrins, solvent effects, transition energies

Porphyrins are highly-absorbing conjugated macrocycles which serve a variety of essential functions in biologically active molecules such as chlorophyll, heme proteins and cytochromes; and which have a range of medicinal, industrial and scientific uses. For these reasons, the mechanisms by which porphyrins respond spectroscopically to various conditions and modifications have long been of vital interest to spectroscopists (Gouterman 1978). For example, the UV-Visible $\pi* \leftarrow \pi$ transition energies of porphyrins and metalloporphyrins have been shown to be sensitive to several properties of solvent environments (Nalliah 1995; Wicks 1994; Renge 1993; Findsen et al. 1988; Nappa & Valentine 1978; Seely & Jensen 1965; Weiss 1972). Further characterization of the response of these bands to specific solvent properties is expected to enhance the use of porphyrins and metalloporphyrins as spectroscopic probes for complex systems such as micelles, sol-gels, and environments in proteins and DNA. These types of studies also have potential uses for industrial applications such the use of porphyrins as photon absorbers in polymer thin films to provide protection from laser radiation (Sayo et al. 1999, Trantolo et al. 1998). In such cases, the environment of the porphyrin can be used to fine-tune the absorption wavelengths.

Solvent effects on the UV-Visible absorption spectra of several types of porphyrins and metalloporphyrins have been investigated previously in limited solvent sets (Nalliah 1995; Wicks 1994; Renge 1993; Renge 1991; Findsen et al. 1988; Nappa & Valentine 1978; Weiss 1972; Seely & Jensen 1965). Porphyrin band energies have been found to respond to the polarizability of the solvent (Nalliah 1995; Wicks 1994; Renge 1993; Renge 1991) indicated by a function of the refractive index such as the Lorentz-Lorenz function and, to a limited extent, the polarity of the solvent (Nalliah 1995; Kolling 1989; Findsen et al. 1988; Nappa & Valentine 1978) indicated by a function of the dielectric constant or other solvent parameters. Kolling analyzed the Soret band energies of nickel protoporphyrin IX dimethyl ester in a set of 16 solvents with varying polarities and varying polarizabilities and concluded, by grouping solvents according to the Chastrette-Purcell generalized classification system, that the dependence of the Soret band energies upon solvent polarizability effects is insignificant (Kolling 1989). However, a more clear-cut distinction of the response to specific solvent properties can be obtained by using solvent sets which have one solvent property varied at a time. Renge studied the spectral responses of porphyrins in a series of nonpolar *n*-alkanes which vary in refractive index, and characterized a definite dependence of the absorption band energies upon the polarizability of the solvent (Renge 1993; Renge 1991). This study extends these investigations

to other types of solvents by using binary mixtures of solvents with similar polarity parameters and dissimilar polarizability parameters, and systematically varying the composition of the mixture.

An occurrence which becomes pronounced in certain mixed solvent systems is preferential solvation, in which the solute is in contact with one solvent to a greater extent than the other. This phenomenon has been modeled extensively based on studies of betaine dyes (Laha et al. 1996; Banerjee et al. 1995; Dawber et al. 1988) and fluorophores (Acree et al. 1994; Acree et al. 1993). When preferential solvation becomes evident based on nonlinear spectral responses to solvent composition (Dawber et al. 1988), it complicates the characterization of the solvent response to the polarizability of the mixture. However, solvent systems which exhibit preferential solvation could be used to model the inner-sphere solvent structures around the porphyrin macrocycle.

In this study, the responses of the porphyrin $\pi* \leftarrow \pi$ transition energies were investigated with respect to changes in the composition of binary solvent mixtures, using nickel and free-base porphyrins with several different peripheral substituents. For mixtures in which preferential solvation is not significant, the responses of the absorption band energies were investigated with respect to functions of the solvent mixture refractive index which relate to the polarizability of the solvent environment. These results allow an empirical verification of solvent effects proposed by previous studies based on sets of pure solvents (Nalliah 1995; Wicks 1994; Renge 1993; Renge 1991).

METHODS

Octaethylporphyrin (H$_2$OEP), nickel octaethylporphyrin (NiOEP), and tetraphenylporphyrin (H$_2$TPP) were obtained from Aldrich and used as received. Protoporphyrin IX dimethyl ester (H$_2$PPDME) and nickel tetraphenylporphyrin (NiTPP) were obtained from Porphyrin Products and Acros, respectively, and used as received. Acetonitrile, chlorobenzene, ethyl acetate, ether (all spectrophotometric grade); nitrobenzene (A.C.S. reagent grade); and anisole (anhydrous) were purchased from Aldrich and used as received. Binary solvent mixtures were made volumetri-

cally using pipets. UV-Visible absorption spectra were obtained with a Perkin Elmer Lambda 3A spectrophotometer having a bandpass of 2 nm or less, using 10 mm and 1 mm glass cuvettes. Porphyrin concentrations were adjusted to give band absorption readings of 1.0 absorbance unit or less (10% transmittance or greater) in order to ensure sufficient transmitted beam intensities for reliable detection. All spectra were blank-corrected with an identical solvent mixture and wavelength-corrected based on the emission lines of the D$_2$ lamp at 656.1 and 486.0 nm. A 12-bit Serial Box Interface manufactured by Vernier Software was used to digitize the voltage signals from the spectrophotometer. Data were sent to a personal computer through a serial port and acquired with Logger Pro data acquisition software (Vernier Software). Data points were taken at intervals of 0.25 nm. Wavelengths of the digitized data were assigned using a calibration macro in Microsoft Excel. Refractive indices of the solvent mixtures were measured using an Abbe C-10 refractometer with a precision of $\pm$ 0.0003 unit. Errors in refractive index measurements caused by evaporation of the more volatile solvent were quantified as described in the Results section. Refractive indices and spectra were obtained at ambient temperatures of 20 $\pm$ 1° C.

RESULTS AND DISCUSSION

Table 1 shows selected solvent parameters for the solvent pairs used for the binary mixtures. The solvents in each pair were chosen to have significant differences in parameters related to polarizability (refractive index, polarizability, molar refraction) and similar polarity parameters (dielectric constant, dipole moment). The solvent pairs were chosen from solvents which dissolve porphyrins having a variety of peripheral substituents, and which are non-coordinating for the metalloporphyrins (nickel porphyrins) used in this study.

The UV-Visible absorption spectra of the free-base porphyrins H$_2$PPDME, H$_2$OEP, and H$_2$TPP, and the metalloporphyrins NiOEP and NiTPP, were obtained as a function of solvent composition for each of the two binary solvent mixtures. The absorption spectra of free-base porphyrins contain a strong Soret band in the blue region and four weaker Q bands in the visible region, while the absorption spectra of metalloporphyrins typically show
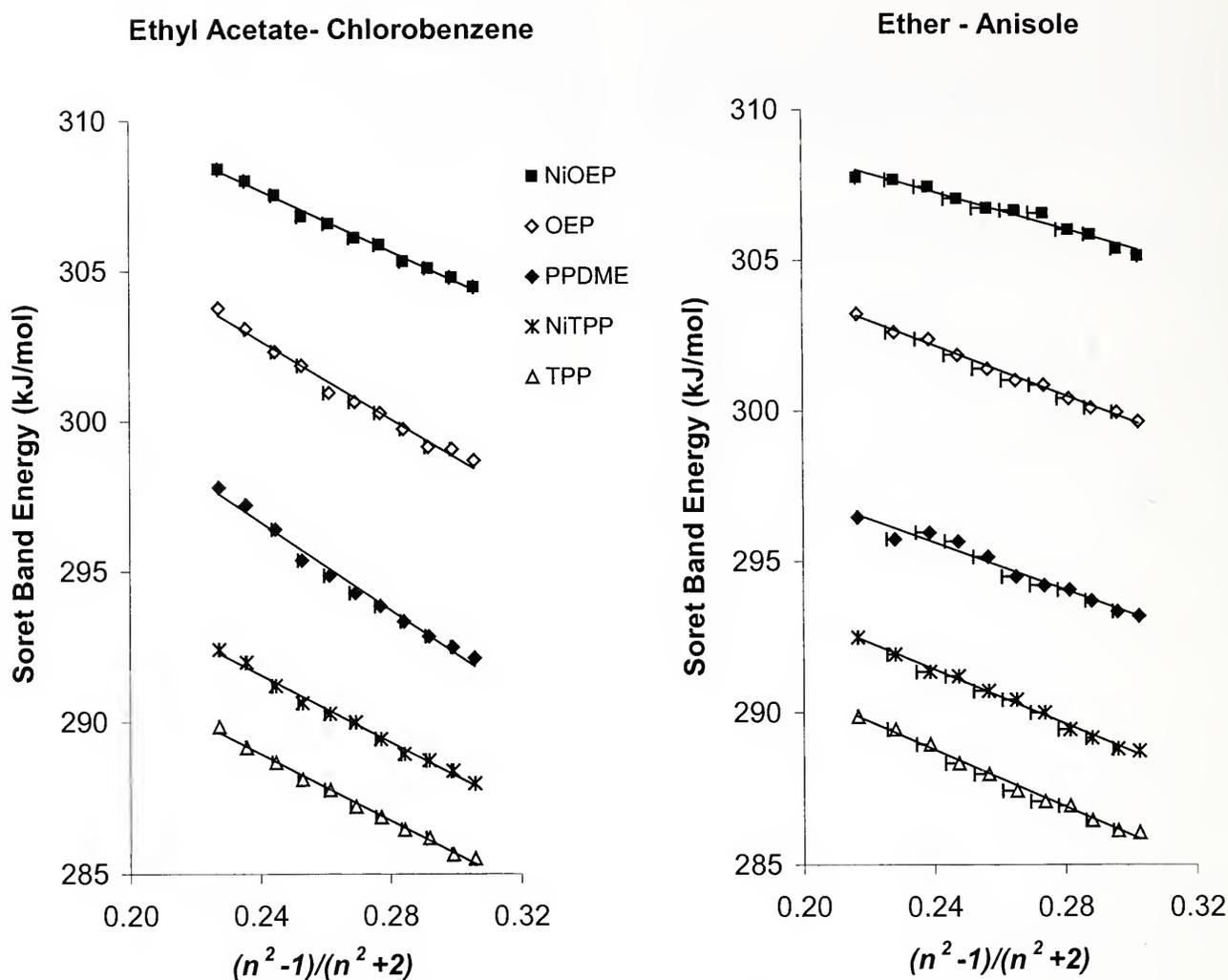
Ethyl Acetate- Chlorobenzene   **Ether - Anisole**

Figure 1.—Soret band energies *vs.* the Lorentz-Lorenz function of refractive index for porphyrins in ethyl acetate – chlorobenzene mixtures and ether – anisole mixtures. Error bars indicate possible errors in refractive index measurements caused by evaporation of the more volatile solvent, as described in the text.

only two Q bands (the α and β bands) in addition to the strong Soret band.

Table 2 shows the correlation coefficients for the Soret band energies with respect to the solvent refractive index for the ethyl acetate – chlorobenzene and ether – anisole mixtures, and with respect to two functions of refractive index which have been related to polarizability (Renge 1993; Renge 1991). The Soret band energies show pronounced linear trends with respect to the refractive index of the solvent mixtures, with correlation coefficient ($|r|$) values rounding to 0.98 or greater. Very similar correlation coefficients are found with respect to functions of refractive index (specifically, the Lorentz-Lorenz function $\phi(n^2) = (n^2-1)/(n^2+2)$ and the function $f(n^2) = (n^2-1)/(2n^2+1)$) which are used in the Bakhshiev and Bayliss equations (Bakhshiev 1972; Bayliss 1950) to relate electronic transition energies to solute-solvent dispersion interac-

tions and solvent polarizability effects (Renge 1991). The Lorentz-Lorenz function is one of the most commonly-used functions relating solvent refractive index to polarizability (Renge 1993; Kolling 1989). Figure 1 shows plots of the energies of the porphyrin Soret bands *vs.* the Lorentz-Lorenz function of the solvent mixture refractive index for the ethyl acetate – chlorobenzene and ether – anisole mixtures.

Since band shifts caused by slight systematic solvent polarity changes are not ruled out in mixed-solvent systems, a causal relationship between the changes in the solvent polarizability and the observed Soret band shifts must be established. First, if the observed Soret band shifts were caused primarily by small changes in solvent polarity rather than by changes in solvent polarizability, Fig. 1 would show opposite slopes for ethyl acetate – chlorobenzene and ether – anisole mixtures, since

Table 1.—Polarizability and polarity parameters for solvents used in this study. Solvents are grouped according to the binary mixtures used. [a] Refractive index values from Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, Second Edition; VCH: New York, 1990. [b] Percentage of the total estimated range for common liquids spanned by the given solvent pair, for the parameter in the previous column. Total estimated ranges were taken from minimum and maximum values in literature tables for each parameter. Δ = 100% × (parameter difference for solvent pair)/(estimated parameter range). [c] Average electric dipole polarizabilities from *The CRC Handbook of Chemistry and Physics*, 72nd ed.; Lide, D.R., Ed.; CRC Press: Boca Raton, 1992. [d] From Schaeffer, C.D., Jr.; Strausser, C.A.; Thomsen, M.W.; Yoder, C.H. (1989). *Data for General, Organic, and Physical Chemistry* [Online]. Available: http://wulfenite.fandm.edu/Data%20/Table_26.html [2000, June 7]. [e] Dielectric constants (relative permittivities) for the pure liquids at 25 °C from Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, Second Edition; VCH: New York, 1990. [f] For the solution dipole moments, temperatures range from 16–25 °C. Measurements apply to either neat liquids or benzene solutions. [g] Dipole moments in Debyes from *Lange's Handbook of Chemistry*, 14th ed.; Dean, J.A., Ed.; McGraw Hill: New York, 1992.

Solvent	n_D^{20} [a]	Δ (%)[b]	Polarizability[c]	Δ (%)[b]	Molar refraction[d]	Δ (%)[b]	ϵ_r [e]	$\Delta(\%)$[b]	μ (D, liq)[f,g]	$\Delta(\%)$[b]	μ (D, gas)[g]	$\Delta(\%)$[b]
Ethyl acetate	1.3719	33	9.7	15	22.3	20	6.02	0.2	1.84	4.8	1.78	1.0
Chlorobenzene	1.5248		13.2		31.2		5.62		1.56		1.72	
Diethyl ether	1.3524	35	9.47	16	22.1	25	4.20	0.07	1.22	0.3	1.15	3.6
Anisole	1.5170		13.1		33.0		4.33		1.24		1.36	

the solvent polarity parameters decrease slightly with increasing refractive index for the former, but increase slightly with increasing refractive index for the latter (Table 1). Second, the Soret band shifts of 3–8 nm (with an average shift of 5.5 nm) observed in this study for solvent refractive index changes of 0.15–0.16 unit compare well in magnitude to the study by Renge of H$_2$TPP in a series of non-polar *n*-alkanes in which a Soret band shift of 3 nm was observed for a refractive index change of 0.08 unit (Renge 1991). Hydrogen bonding effects are highly unlikely for all solvents in this study. Therefore the observed Soret band shifts can be attributed mainly to changes in the solvent polarizability.

Error bars in Fig. 1 depict possible errors in experimental refractive index measurements caused by evaporation of the more volatile solvent during the measurement, the magnitude of each error bar having been calculated by assuming the actual refractive index of the mixture to be a linear function of solvent volume percent. As shown in Fig. 1, the measured refractive indices of the ether – anisole mixtures at intermediate compositions have the most pronounced systematic deviations from the expected values. Nevertheless, these experimental deviations change the correlation coefficients in Tables 2 and 3 by less than 0.01 for the Soret and Q$_y$ bands, and by less than 0.04 for the less highly-correlated Q$_x$ bands. The deviations in refractive index attributed to preferential evaporation for the ethyl acetate – chlorobenzene mixtures are significantly less than for the ether – anisole mixtures, as shown by the error bars in Fig. 1.

In addition to the Soret band energies, the energies of several porphyrin Q bands also show correlations with respect to the refractive index of the ethyl acetate – chlorobenzene and ether – anisole mixtures (Table 3). In accordance with Renge, we have observed that the Q bands undergo smaller shifts with respect to solvent refractive index than do the Soret bands (Renge 1993). Renge has attributed the shifts of the porphyrin $\pi^* \leftarrow \pi$ band energies with respect to solvent refractive index largely to the increase in polarizability of the porphyrin electronic excited state with respect to the ground state, which becomes larger with increasing transition energy and intensity (Renge 1993; Renge 1991). Therefore the Q bands, having lower transition energies and intensities, should be less responsive to changes in solvent refractive index than the Soret band; and the Q$_x$ bands should be less responsive to solvent refractive index than the Q$_y$ bands for the same reason. Accordingly, for the free-base porphyrins in this study, the Q$_y$ bands show substantially higher correlations

Table 2.—Correlation coefficients of Soret band energies with respect to polarizability functions of the solvent refractive index in binary solvent systems. The sign of the correlation coefficient indicates the sign of the slope. [a] Lorentz-Lorenz function $\phi(n^2) = (n^2 - 1)/(n^2 + 2)$. [b] $f(n^2) = (n^2 - 1)/(2n^2 + 1)$.

	Ethyl acetate–chlorobenzene			Ether–anisole		
	Refractive Index	$\phi(n^2)$[a]	$f(n^2)$[b]	Refractive Index	$\phi(n^2)$[a]	$f(n^2)$[b]
H_2OEP	−0.992	−0.993	−0.995	−0.996	−0.997	−0.997
H_2TPP	−0.996	−0.997	−0.998	−0.995	−0.996	−0.997
H_2PPDME	−0.992	−0.994	−0.996	−0.985	−0.984	−0.983
NiOEP	−0.996	−0.997	−0.997	−0.984	−0.982	−0.979
NiTPP	−0.995	−0.996	−0.997	−0.997	−0.996	−0.996

($|r| = 0.94$ or greater) with respect to solvent refractive index than the Q_x bands, with the Q_x bands also showing inconsistencies in the signs of the slopes, as indicated by the signs of the correlation coefficients in Table 3. The poorer correlations of the Q_x band energies observed in this study with respect to solvent refractive index are likely to be caused in part by instrumental limitations in observing small band shifts, and may be also related to the relative magnitudes of the electronic interactions which influence these bands. The anomalously positive slopes of several of the Q_x band energies with respect to solvent refractive index in the ether–anisole mixtures are most likely to be caused by slight solvent polarity effects (resulting from the small polarity differences between solvents in the mixture) canceling the small polarizability effects on the Q_x bands (Renge 1993).

In this study, only band maxima were recorded; and band widths and asymmetry were not taken into account. Therefore it is possible that the band shifts may be reflecting a combination of solvent effects, including small amounts of dimerization in certain solvents. These combined solvent effects may also contribute to deviations from linearity with respect to solvent polarizability functions.

The occurrence of preferential solvation of a solute in a solvent mixture may be determined based on the curvature of the band energies with respect to the solvent mole fraction (Dawber et al. 1988). In the ethyl acetate – chlorobenzene and ether – anisole mixtures, the Soret band energies show linear trends with respect to the solvent mole fraction, with $|r|$ values of 0.99. Although very slight curvature is discernable in plots of the Soret band energies vs. solvent mole fraction for the ethyl acetate – chlorobenzene mixtures, the linear trends indicate that preferential solvation has either a slight or negligible effect in the ethyl acetate – chlorobenzene and ether – anisole mixtures.

Porphyrin absorption spectra were also obtained in acetonitrile – nitrobenzene mixtures. Plots of porphyrin band energies vs. solvent

Table 3.—Correlation coefficients of Q-band energies with respect to the solvent refractive index in binary solvent systems. The sign of the correlation coefficient indicates the sign of the slope. See text for explanation of positive slopes.

	Ethyl acetate–Chlorobenzene				Ether–Anisole			
	$Q_y(0,1)$	$Q_y(0,0)$	$Q_x(0,1)$	$Q_x(0,0)$	$Q_y(0,1)$	$Q_y(0,0)$	$Q_x(0,1)$	$Q_x(0,0)$
H_2OEP	−0.987	−0.990	−0.852	−0.776	−0.987	−0.986	0.858	0.901
H_2TPP	−0.941	−0.991	−0.917	−0.963	−0.996	−0.995	−0.749	−0.691
H_2PPDME	−0.959	−0.973	−0.864	−0.870	−0.980	−0.989	0.616	0.767
	$Q(0,1)$	$Q(0,0)$			$Q(0,1)$	$Q(0,0)$		
NiOEP	−0.986	−0.977			−0.945	−0.901		
	Q				Q			
NiTPP	−0.958				−0.964			

mole fraction in these mixtures showed pronounced curvature; however, spectral evidence indicated that the curvature could have been at least partially caused by porphyrin decomposition in nitrobenzene. Therefore the acetonitrile – nitrobenzene data were excluded from this study, pending further investigations of this system.

CONCLUSIONS

The Soret band energies of three free-base porphyrins and two nickel porphyrin complexes show highly linear correlations with respect to the Lorentz-Lorenz function of the solvent refractive index in ethyl acetate – chlorobenzene and ether – anisole binary solvent mixtures. While it may be argued that the observed band shifts in this mixed-solvents study are not completely uninfluenced by slight systematic solvent polarity changes throughout the series of mixtures, a causal relationship between changes in the solvent polarizability and the observed Soret band shifts is verified by: 1) the consistency in the direction of the Soret band shifts with respect to solvent refractive index regardless of whether the polarity of the mixture slightly increases or decreases with increasing refractive index, and 2) the consistency in the magnitudes of the Soret band shifts with respect to changes in solvent refractive index in both this mixed-solvent study and a study of H_2TPP in a series of non-polar n-alkanes (Renge 1991). These studies affirm the contribution of solvent polarizability effects to solvent influences on the band energies of porphyrins and metalloporphyrins, in contrast to an analysis in which it was concluded that solvent polarizability has no major effect upon the Soret band energies of NiPPDME (Kolling 1989). The significance of the solvent polarizability influence on the Soret band energies is affirmed by comparing magnitudes of the Soret band shifts of 3–8 nm observed in this study, in solvents with similar polarities and different polarizabilities (with refractive index changes of 0.15–0.16 unit), to those of Kolling's analysis, in which a maximum Soret band shift of 8 nm was observed for NiPPDME in a set of 16 solvents which varied substantially in polarity as well as polarizability (with refractive index changes of up to 0.23 unit) (Kolling 1989). This mixed-solvents study indicates that for the Soret and Q_y bands, the polarizability ef-

fects of the solvent must be taken into account for an accurate analysis of the total solvent effects upon the transition energies of porphyrins. These characterization studies are applicable to the development of porphyrins as spectroscopic probes of specific environments and as photon absorbers in industrial applications.

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