Stabilization of donor–acceptor complexes formed by associated porphyrins in thin films

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Abstract

The tetraphenylporphine amino derivatives meso-tetra(p-aminophenyl)porphine and meso-tetra(N,N-dihexadecyl-4-aminophenyl)porphine were investigated using ultraviolet and visible (UV) and infrared (IR) absorption spectroscopy in thin films. Porphyrins forming associated species in solution were shown to be strongly solvated. This peculiarity allows one to prepare thin films by solvent evaporation from solution instead of by crystallization of tetraphenylporphine. The appearance of a new broad band in the red and near-IR region is revealed in the UV spectra of both aminoporphyrins. This band is evident only in the presence of water traces in the thin film. The changes observed in the UV and IR spectra of meso-tetra(p-amino-phenyl)porphine thin films in the presence of water traces, as compared with water-free thin films, are interpreted via the formation and stabilization of a donor–acceptor complex in its associated form. According to the IR spectra, water molecules participate in the formation of the solvation shell and donor–acceptor complex.

Keywords: Donor–acceptor complexes; Porphyrin associates; Intermolecular interactions; Thin films; Absorption ultraviolet, visible and infrared spectroscopy

1. Introduction

Intermolecular interactions between porphyrins in dimeric and associated species are widely investigated to understand and reproduce the mechanisms of interaction of pigments within the chromophore complex of the photosynthetic reaction centre [1–7]. Strongly coupled dimeric porphyrin complexes are of great interest because their absorption spectra have a broad band shifted to the red region relative to the electronic transition $^1Q(\pi,\pi^*)$ of the corresponding monoporphyrin [8,9]. Usually the broad band occupied the red and near-IR region of the spectrum. In some cases this band is interpreted via the delocalization of molecular orbitals over the whole π system due to a significant contribution of the charge transfer configuration [8–10]. Porphyrin complexes with similar optical characteristics can also be obtained by molecular association [11,12]. In this case, donor–acceptor interactions in dimers or associates may arise owing to the presence of functional groups attached to porphyrin molecules when achievement of favourable conditions for their realization is possible.

Compared with other porphyrins, amino derivatives of tetraphenylporphine are characterized by a number of unique features, as evidenced by studying the absorbance and luminescence properties of their associated species. Intermolecular interaction and specific features of association of

porphyrins in solution as well as under immobilization in copolymer were investigated using absorbance, luminescence and vibrational spectroscopy [12]. The appearance of the above-mentioned broad band in the red and near-IR region was revealed by studying the association of an amino derivative in thin films.

In this work the association of tetraphenylporphine amino derivatives in thin films and the conditions of formation of donor–acceptor complexes in associated porphyrin species were studied using ultraviolet and visible (UV) and infrared (IR) absorption spectroscopy. The role of water in the formation of these complexes was examined.

2. Experimental details

Synthesis of the compounds shown in Scheme 1 was described elsewhere [13–15]. Dimethylformamide (DMF),

Porphyrin I : R_{1-4} —⟨O⟩

Porphyrin II : R_{1-4} —⟨O⟩—NH_2

Porphyrin III: R_{1-4} —⟨O⟩—N⟨$C_{16}H_{33}$ / $C_{16}H_{33}$
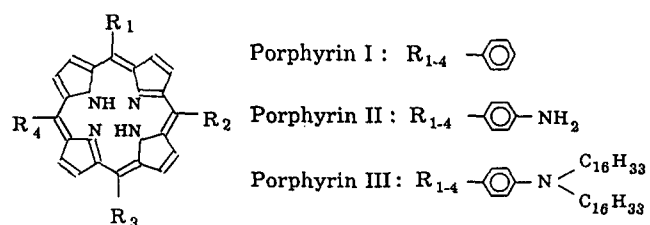
Scheme 1. Compounds studied.

dioxane and other organic solvents used were purified by conventional methods [16]. Organic solvents were dried using a "4A" molecular sieve. Solid porphyrin was dried by heating at 110 ± 5 °C for 3 h. Thin films of associated porphyrins were prepared by solvent evaporation from their solutions until complete disappearance from a CaF_2 plate surface. Hydration of porphyrin thin films was performed by keeping them at high humidity for 4 days.

The UV absorption spectra of porphyrin solutions and thin films were obtained with Specord M-40 and Hitachi 557 spectrophotometers. The IR spectra of thin films and porphyrins in the solid state in KBr or as a suspension in vaseline oil were recorded with Specord M-80 or UR-20 spectrophotometers. All measurements were performed at 298 K. To compare the intensities of absorption bands, their optical densities were normalized with respect to the optical density of the 1350 cm^{-1} band, which is characteristic in tetraphenylporphines [17].

3. Results

3.1. Specific features of porphyrin association in thin films

Fig. 1 shows the UV spectra of associated Porphyrin II in DMF (Fig. 1A, curve 1) and in thin films prepared by solvent evaporation from solution (Fig. 1B). For comparison, the UV spectrum of monomeric tetraphenylporphine (Porphyrin I) in the same solvent is also presented (Fig. 1A, curve 2).
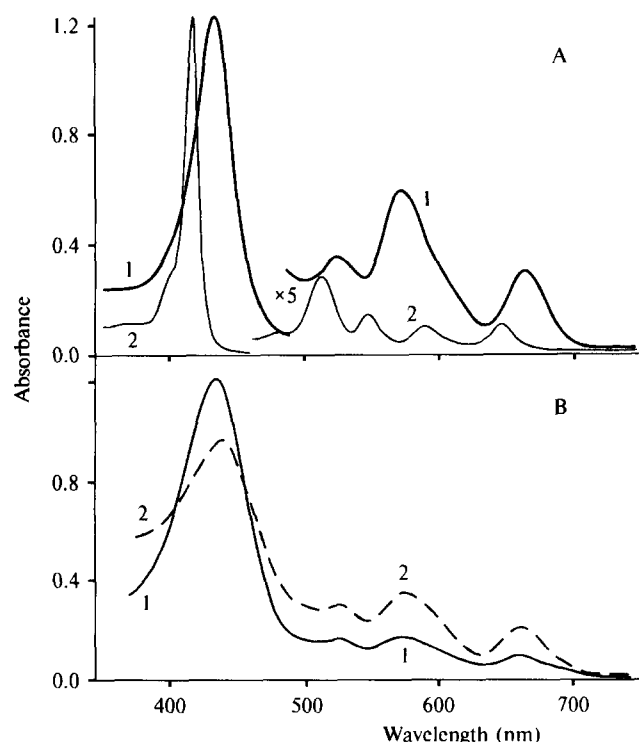

Fig. 1. Absorption spectra of (A) Porphyrin II (1) and Porphyrin I (2) in DMF and (B) Porphyrin II in thin films (films 1 and 2 were prepared with different initial concentrations of porphyrin in solution).

Let us note that the amino derivatives of porphyrin, i.e. Porphyrin II and Porphyrin III, are strongly solvated in solution, as evidenced by the experimental data obtained in this work. This allows one to prepare thin films of these porphyrins, in contrast with monomeric Porphyrin I which is crystallized under solvent removal from its solution. As follows from the UV spectra, the molecules of Porphyrin II are associated both in solution and in thin films. Furthermore, the higher the initial concentration of the porphyrin in the solution used for the preparation of the thin film, the higher is the degree of porphyrin association in the film (Fig. 1B). In the UV spectrum (Fig. 1B, curve 1) the Soret band becomes broader, its extinction coefficient decreases and its maximum is red shifted by 3–4 nm with respect to the Soret band of porphyrin solution when $\lambda_{max} = 430$ nm (Fig. 1A, curve 1). Similar changes are observed in the UV spectrum at a higher degree of association (Fig. 1B, curve 2): a further broadening of the Soret band, a decrease in its extinction coefficient and a red shift of its maximum by 5–6 nm with respect to curve 1. Moreover, a marked increase in absorption in the region of quasi-allowed electronic transitions Q_y and Q_x is observed in the approximately 500–700 nm region of the UV spectrum (curve 2) as compared with curve 1. This increase in absorption appears to be proportional to the increase in porphyrin concentration in a thin film containing no water.

The IR spectra presented in Fig. 2 show that the properties of Porphyrin II in the solid state are similar to the properties of porphyrin thin film as compared with those of Porphyrin I without amino groups in the phenyl rings. First of all, note worthy is the doublet, which is characteristic of the tetrapyrrole macrocycle in tetraphenylporphines. The latter involves two bands at 1440 and 1473 cm^{-1}. In the corresponding IR spectrum of Porphyrin I the intensities of these bands are almost identical (curve 1). However, the intensity of the 1440 cm^{-1} band in the IR spectrum of Porphyrin II is very weak, but the 1473 cm^{-1} band has a strong intensity (curves 2 and 3). In the region of valence vibrations of N–H groups in the IR spectrum of Porphyrin II the bands of symmetrical and asymmetrical vibrations of amino groups are observed at 3362 and 3450 cm^{-1} respectively. The intensity of the bands increases noticeably in thin films as compared with the solid state. The band associated with imino group vibrations in the pyrrole ring observed in the IR spectrum of Porphyrin I at 3315 cm^{-1} (curve 1) is shifted by 95 cm^{-1} towards the low frequency region in the corresponding IR spectrum of Porphyrin II (curves 2 and 3).

The bands of valence vibrations of C–H groups conjugated in the porphyrin macrocycle are observed in the IR spectrum of Porphyrin I at 3020 and 3056 cm^{-1} (Fig. 2, curve 1). In contrast, the IR spectrum of Porphyrin II shows that these bands are shifted towards the low frequency region and are apparently split because of intermolecular interactions. As a result, the bands of valence vibrations of methylene groups are observed at 2856, 2924 and 3020 cm^{-1} (curve 2). In the IR spectrum of Porphyrin II thin film (curve 3) these bands become more intense as compared with Porphyrin II in the
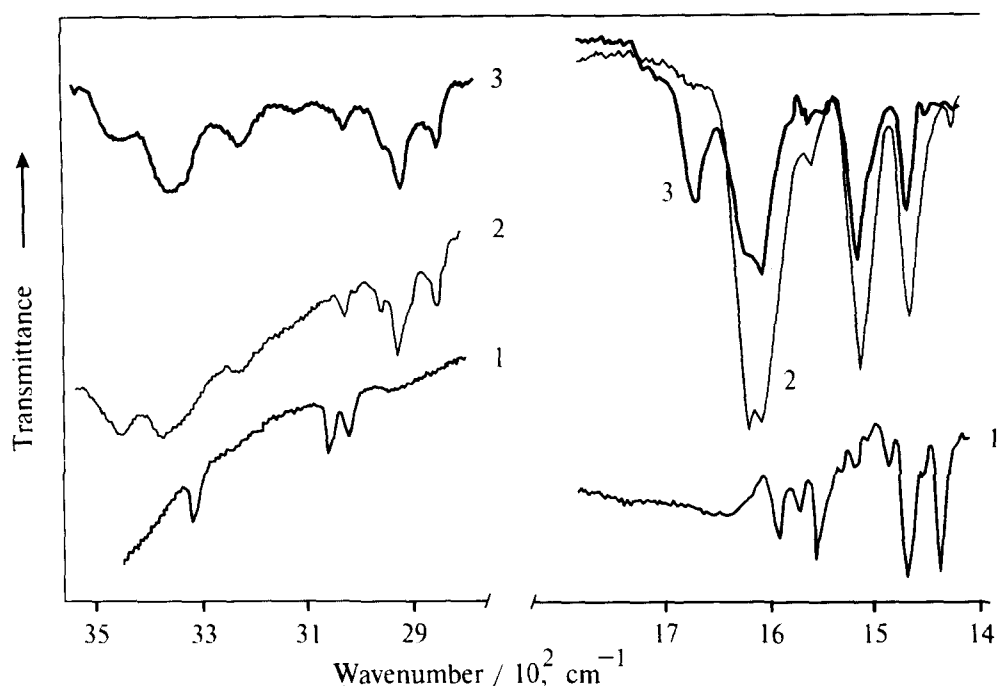
Fig. 2. Infrared spectra of Porphyrin I (1) and Porphyrin II (2, 3) in KBr (1, 2) and in thin film (3).

solid state (Table 1). Furthermore, a new band is observed in the same spectral region at about 3120 cm^{-1} in the IR spectrum of Porphyrin II thin film. Another new band in this spectrum at 1667 cm^{-1} is attributed to the solvent, i.e. dimethylformamide [18]. The band is preserved even in the case of solvent removal from the porphyrin solution at 100 °C. This evidence allows one to conclude that solvent molecules are strongly bonded with associated porphyrin both in solution and in thin film, forming a solvation shell.

The bands of deformational vibrations of phenyl rings attached to the porphyrin macrocycle are observed at 1556,

Table 1
Some band characteristics in IR spectra of porphyrins

Frequency ν (cm^{-1})	Porphyrin II		Porphyrin I Absorption A_ν in KBr
	Absorption A_ν [a] in water-free film	Absorption A_ν in KBr	
736 (728) [b]	–	0.63	2.5
804 (800)	–	1.3	4.1
850 (843)	–	0.58	0.49
1180	–	1.67	0.90
1350	1	1	1
1440	0.44	0.16	1.6
1470	1.75	0.87	1.6
1516	3.5	1.3	0.38
2856	0.65	0.47	–
2924	1.20	0.69	–
3020	0.48	0.22	0.67
3220	0.58	0.23	–
(3315)	–	–	0.70

[a] The absorption of bands, A_ν, is normalized to that of the 1350 cm^{-1} band;
[b] the frequencies given in parentheses are observed in the IR spectrum of Porphyrin I.

1571 and 1592 cm^{-1} in the IR spectrum of Porphyrin I. In the IR spectrum of Porphyrin II the bands at 1571 and 1592 cm^{-1} are overlapped with the bands of very strong intensity at 1604 and 1618 cm^{-1}, which are attributed to deformational vibrations of amino groups. The only exception is provided by the 1556 cm^{-1} band, which was also observed in the IR spectrum of Porphyrin II.

Hence, according to the UV spectra, association of Porphyrin II has no effect on the structure of its electronic transitions at high degrees of association in water-free thin films. However, marked changes in electronic structure in the region of quasi-allowed electron transitions are observed as compared with Porphyrin I. Hence the UV spectrum of Porphyrin II shows four bands, including the Soret one. The IR spectroscopy data also show that the vibrational characteristics of Porphyrin II change considerably as compared with those of Porphyrin I. The changes in the vibrational characteristics of the porphyrin macrocycle result in the development of another vibrational structure, which is different from the structure of the porphyrin macrocycle in Porphyrin I. The changes are likely to be related to intermolecular interactions resulting in association of Porphyrin II molecules.

3.2. Formation of donor–acceptor complexes by associated porphyrins

The UV spectra of the porphyrin thin films show considerable changes in the state of associated species in the presence of water traces in the solution used for thin film preparation. A broad absorption band with a high extinction coefficient at $\lambda_{max} \approx 800$ nm and $\Delta\lambda_{1/2} = 120$ nm ($\Delta\lambda_{1/2} \approx 2000$ cm^{-1}) is observed in the UV spectrum of Porphyrin III thin film in the presence of minor amounts of water (Fig. 3,
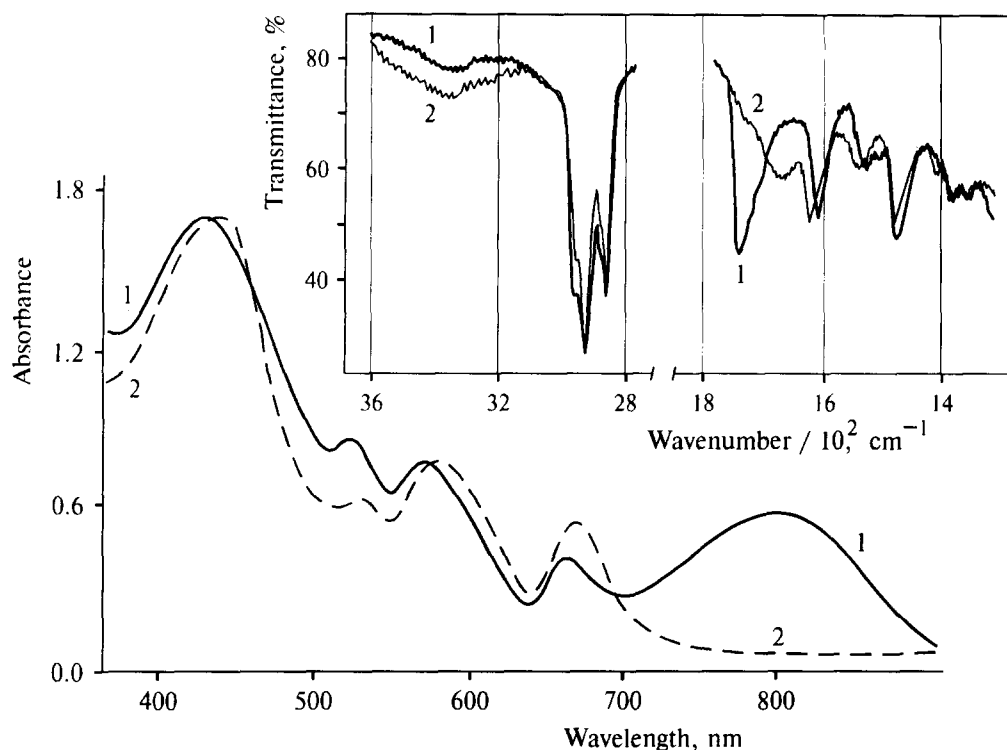
Fig. 3. Absorption spectra of Porphyrin III in thin films with minor amounts of water prepared by evaporation of porphyrin in dioxane (1) and in CCl₄ (2). The inset shows IR spectra of the same films.

curve 1). The broad band was assigned to a charge transfer band which appears as a result of the formation of a charge transfer complex between associated porphyrin molecules [19]. In the approximately 670–900 nm region the band was absent when triethylamine (TEA) or CCl_4 was used as solvent, which are known to be electron-donating and electron-accepting compounds respectively with respect to porphyrin. In this case, water traces have no effect on the state of associated forms of porphyrin (curve 2). The band seen in the UV spectrum of Porphyrin III is also observed when other solvents are used for the preparation of thin films, such as acetone, dimethylformamide, diethyl ether, ethanol, pyridine, etc.

The appearance of the charge transfer band in the UV spectrum of Porphyrin III thin film is accompanied by the occurrence of a new intensive band at 1740 cm^{-1} in the IR spectrum (Fig. 3, inset, curve 1). The band is shifted to 1748 cm^{-1} when the polar organic solvent DMF is used for thin film preparation. As the water content changes, the optical density of the 1740 cm^{-1} band is proportional to the optical density of the band in the UV spectrum at $\lambda_{max} = 800$ nm [19]. The correlation coefficient between optical densities is 0.95. The appearance of the charge transfer band is also accompanied by other marked changes in the IR spectra: a decrease in absorption in the approximately 3100–3600 cm^{-1} region, a broadening of the bands at 2858 and 2928 cm^{-1}, a shift of the 1618 cm^{-1} band by 11 cm^{-1} towards the low frequency region, etc. (curves 1 and 2). The strong bands at 2858 and 2928 cm^{-1} in the IR spectrum of Porphyrin III are associated with the vibrations of the C–H groups in hexadecyl

groups and the porphyrin macrocycle. In this region a shoulder is also observed at 2960 cm^{-1}.

The presence of water traces in the solvent used for the preparation of Porphyrin II thin films is also associated with
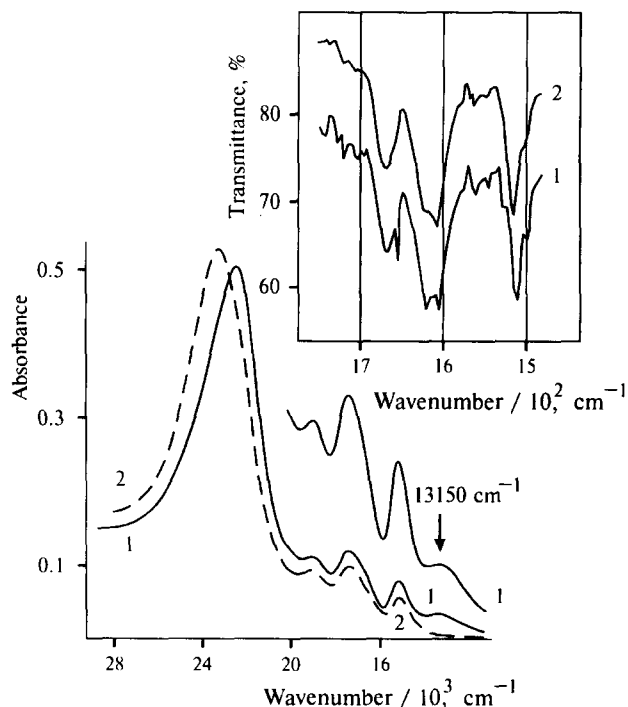

Fig. 4. Absorption spectra of Porphyrin II in thin films prepared by evaporation of porphyrin in DMF in the presence (1) and in the absence of minor amounts of water (2). The inset shows IR spectra of the same films.

considerable changes in the UV spectrum (Fig. 4, curve 1; for comparison, see curve 2). The most pronounced changes (curve 1) are related to the appearance of the band in the red and near-IR region at $\lambda_{max} \approx 13\ 150\ cm^{-1}$ (760 nm) and the increase in absorption in the region of quasi-allowed electron transitions as compared with the UV spectrum (curve 2). However, the IR spectra of the same films of Porphyrin II do not show considerable changes (Fig. 4, inset, curves 1 and 2). Noteworthy are the band at 1655 cm^{-1} and the maximum at 1618 cm^{-1} in the IR spectrum of the film with minor amounts of water (curve 1), which are absent in the IR spectrum of the water-free film (curve 2).

The IR spectroscopy data show that an interaction characteristic of associated Porphyrin II molecules takes place in thin films and probably also in the solid state. An increase in the intensity of Porphyrin II bands as compared with those of Porphyrin I is also observed in the other region of the IR spectrum (Fig. 5). The most pronounced increase in the IR spectrum of Porphyrin II is observed for the 1180 and 1516 cm^{-1} bands (Table 1). In contrast, the relative intensity of the 804 and 736 cm^{-1} bands associated with the γ vibrations of the C–H and N–H groups of the porphyrin macrocycle [20] decreases considerably in the IR spectrum of Porphyrin II as compared with that of Porphyrin I. Furthermore, the IR spectrum of Porphyrin II has two new bands: the band with a weak intensity at 1130 cm^{-1} and the broad band with a strong intensity at 1285 cm^{-1}.

Numerous investigations of porphyrins have shown that the band in the 1280–1290 cm^{-1} region is usually observed

Fig. 5. Infrared spectra of Porphyrin I (1) and Porphyrin II (2) in KBr.

in the IR spectrum of the porphyrin radical cation [21,22]. If the appearance of the 1285 cm^{-1} band is attributed to the radical cation, then molecular oxygen is an oxidizing agent. The presence of the superoxide radical $O_2^{\cdot-}$ associated with the 1053 cm^{-1} band [22,23] is evidenced by the shoulder at 1060 cm^{-1} (Fig. 5, curve 2). The absence of a sharp band is likely to be related to the broadening of the neighbouring band at 1070 cm^{-1}.

Hence the results presented above show that the changes in the absorption spectra in the presence of minor amounts of water in thin films of associated Porphyrin III are related to the formation of a charge transfer complex. Similar changes in the presence of water traces are also observed in thin films of associated Porphyrin II. In connection with this, the role of water in the intermolecular interaction of Porphyrin II and the effect of water on the properties of porphyrin thin films were investigated in more detail.

3.3. Participation of water molecules in formation of donor–acceptor complexes

To study the IR spectra in more detail, thin films of Porphyrin II with maximal concentration of porphyrin were prepared. An increase in concentration is associated with an increase in the degree of porphyrin association in the thin film (Fig. 6; see the spectra shown in Fig. 1B). The presence of minor amounts of water results in changes in the structure of the UV spectrum at a higher degree of porphyrin association as compared with films without water. A new band in the red and near-IR region and a higher absorption in the region of quasi-allowed electron transitions Q_y and Q_x (Fig. 6, curve 2) are observed in the films with minor amounts of water as compared with films without water (curve 1).

The IR spectra of all three films show the 1285 cm^{-1} band, which is present both in thin films and in the solid state (Fig. 7). The IR spectra of the films in the presence and absence of minor amounts of water (Fig. 7, curves 1 and 2) are similar. However, they show some differences. In the case of the IR spectrum of curve 1 the ratio between the intensities of the 1440, 1404 and 1384 cm^{-1} bands is different from the ratios of these bands in the IR spectra of curves 2 and 3. Moreover, the shoulder is observed only at 1618 cm^{-1} (Fig. 7, inset, curve 1). In contrast, the IR spectrum of the film with minor amounts of water shows a maximum at 1618 cm^{-1} and a shoulder at 1653 cm^{-1} (Fig. 7, inset, curve 2 and Fig. 6, inset, curve 1 respectively), whereas in the case of the IR spectrum of the water-free film the shoulder at 1653 cm^{-1} is almost absent. The characteristics of some bands in the water-free film and in films with minor amounts of water are presented in Table 2.

Hydration of the film containing minor amounts of water results in a certain increase in absorption in the 670–800 nm region with λ_{max} at about 750 nm (about 13 300 cm^{-1}) (Fig. 6, curve 3). Some changes are also observed in the IR spectrum; in particular, the two bands at 1440 and 1384 cm^{-1} practically disappear (Fig. 7, inset, curves 2 and 3). Furthermore, the intensity of the narrow band at 1557 cm^{-1} shows
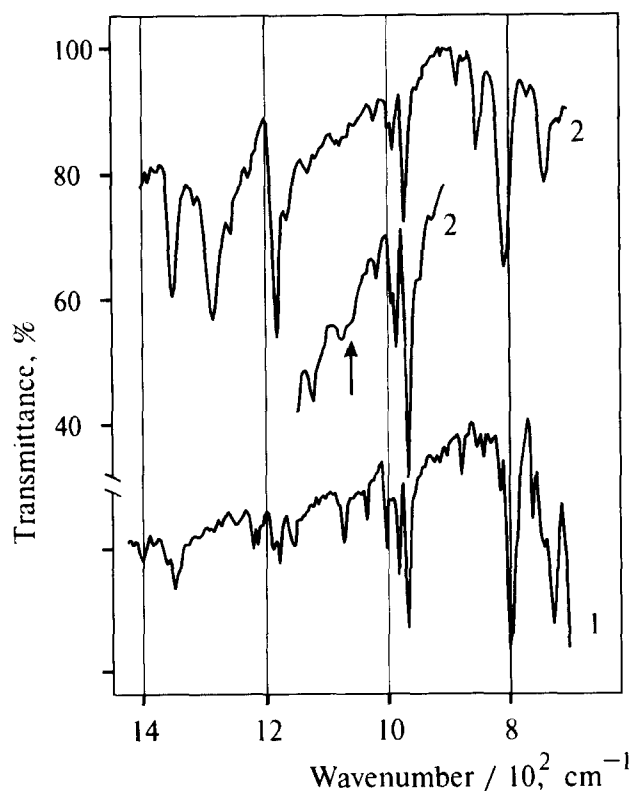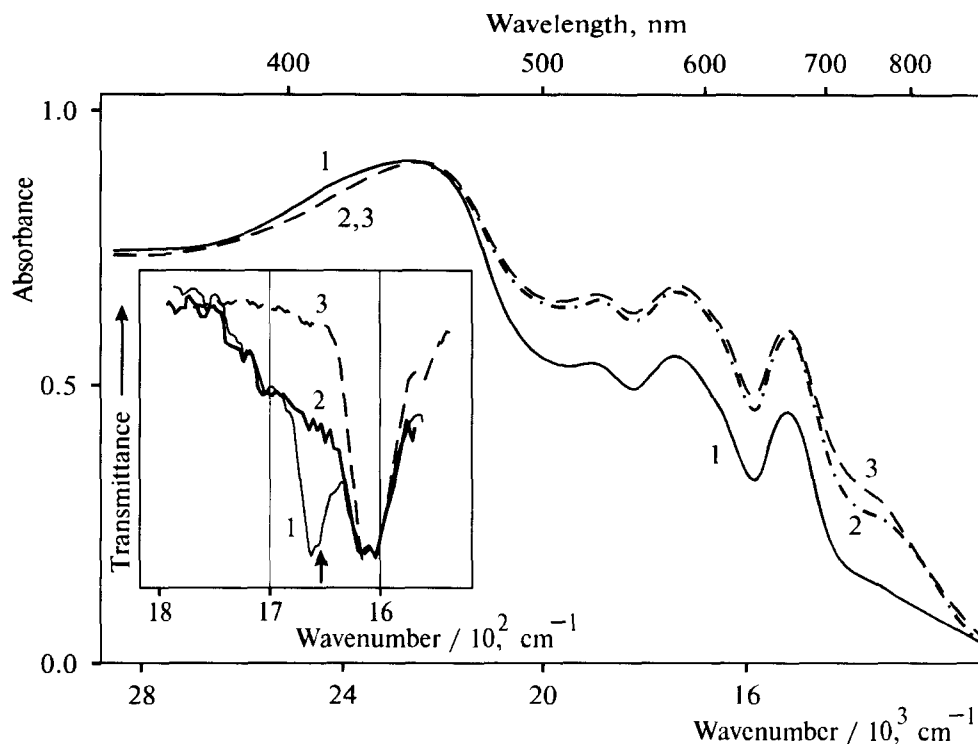
Fig. 6. Absorption spectra of Porphyrin II in thin films prepared by evaporation of porphyrin in DMF in the absence (1) and in the presence of minor amounts of water (2) and after hydration of the latter film (3). The inset shows IR spectra of Porphyrin II in thin films (1, 2) and in KBr (3) in the presence of minor amounts of water (1) and after hydration of the film (2).

a marked increase with respect to the bands of the porphyrin macrocycle at 1473 and 1350 cm^{-1} (Fig. 7, compare curves 2 and 3). The band of DMF at 1667 cm^{-1} disappears as a result of hydration (Fig. 6, inset, curve 2). However, the absorption in the 1620–1750 cm^{-1} region, which is high as compared with the solid state of Porphyrin II, is preserved (Fig. 6, inset, compare curves 2 and 3).

Hydration of the film without water also leads to a certain decrease in the intensity of the two bands at 1440 and 1384 cm^{-1} and the disappearance of the 1667 cm^{-1} band. However, the maximum at 1618 cm^{-1}, which is characteristic of all IR spectra of Porphyrin II containing minor amounts of water, does not appear. As in the initial film, the same shoulder is preserved at the above frequency, even though hydration of the film without water takes place.

Drying of Porphyrin II in the solid state results in the appearance of new maxima of the broad bands in the IR spectrum and a decrease in the intensity of some bands, including those of the deformational vibrations of amino groups. Hence the maxima at 1593 and 1600 cm^{-1} are observed in this region as a result of drying (Fig. 8). A strong
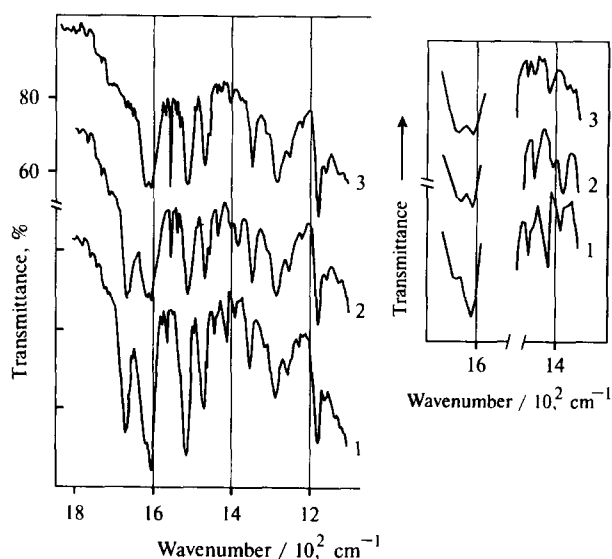

Fig. 7. Infrared spectra of Porphyrin II in thin films prepared by evaporation of porphyrin in DMF in the absence (1) and in the presence of minor amounts of water (2) and after hydration of the latter film (3). The inset shows two regions of the same IR spectra.

Table 2
Characteristics of bands associated with N–H vibrations of amino and imino groups of Porphyrin II thin films

Frequency ν (cm^{-1})	Absorption A_ν [a] in water-free film	Absorption A_ν in film with traces of water
1604 (deformational, symmetric) [b]	4.7	1.6
1618 (deformational, asymmetric) [b]	2.9	1.6
3220 (valence) [c]	0.58	0.48
3362 (valence, symmetric) [b]	1.2	0.92
3450 (valence, asymmetric) [b]	0.47	0.50

[a] The absorption of bands, A_ν, is normalized to that of the 1350 cm^{-1} band; [b] vibrations associated with N–H bonds of amino groups; [c] vibration associated with N–H bonds of imino groups.
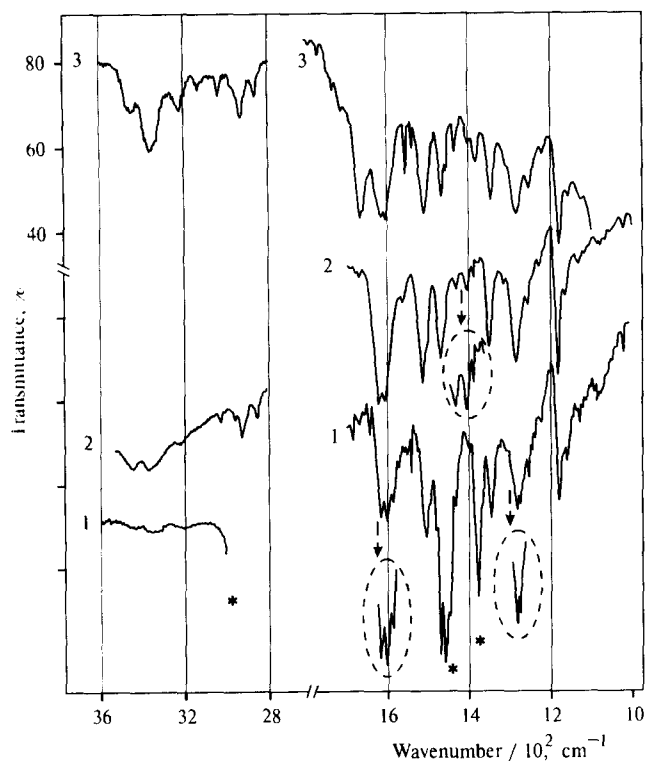
Fig. 8. Infrared spectra of Porphyrin II in vaseline oil after drying (1), in KBr (2) and in thin film with minor amounts of water prepared by evaporation of porphyrin in DMF (3). The bands of vaseline oil are marked with asterisks.

decrease in the absorption of N–H groups is also observed in the region of the valence vibrations at 3450 and 3360 cm^{-1} as a result of porphyrin drying (see curves 1 and 3). In the region of the band assigned to the porphyrin radical cation, two maxima at 1273 and 1280 cm^{-1} are also observed. The marked decrease in the intensity of these bands as a result of porphyrin drying, as compared with hydrated thin films, shows that the appropriate groups of atoms are strongly hydrated in the presence of minor amounts of water.

Hence the data show that two components of the IR maximum are revealed, as a result of drying, in the broad bands at 1604 and 1285 cm^{-1}. The groups of atoms corresponding to these frequencies are hydrate even in the solid state of porphyrin. The increase in the intensity of the bands in the region of these frequencies suggests a strong polarization of the bonds between certain groups of atoms as a result of selective binding of solvent molecules. The changes in the IR spectra observed in the film containing minor amounts of water, as compared with the film without water, are accompanied by the appearance of a new band in the UV spectrum in the red and near-IR region with its maximum at about 760 nm and an increase in absorption in the region of quasi-allowed electron transitions.

4. Discussion

The association of Porphyrin II in solution and in thin water-free films shows that the structure of electronic tran-

sitions of associated porphyrin in the films remains virtually unchanged, according to the UV spectra, despite a significant increase in association degree. At the same time the data of IR spectroscopy show that the vibrational structure of the Porphyrin II macrocycle in thin films appears to be similar to the structure of porphyrin in the solid state but quite different from the structure of Porphyrin I. This fact suggests that a similar intermolecular interaction also takes place in the solid state of Porphyrin II. From this point of view, the formation of thin films by solvent removal from porphyrin solution is probably related to intermolecular interaction rather than Porphyrin I crystallization. The interaction resulting in the association is so strong that monomer species of Porphyrin II are not identified. The only exception is provided by porphyrin immobilization in poly (methacrylic acid) with a high content of methacrylic chains with respect to porphyrin pigment, where more than 90% of Porphyrin II was found as monomer species [24]. In connection with this, the origin of the intermolecular interaction, the solvation of porphyrin in thin films and the effect of water on this interaction are the most important problems.

The amino derivatives Porphyrin II and Porphyrin III have a similar nature of association in thin films, as evidenced by the results presented above. However, there is some difference in the structures of the donor–acceptor complexes with different lateral groups attached to the phenyl rings (see Scheme 1). The configuration of the charge transfer complex was characterized in the presence of water traces in thin films of Porphyrin III. The presence of eight hexadecyl groups in each porphyrin molecule is favourable for realization of the charge transfer configuration. Realization of the configuration in the porphyrin associate is accompanied by changes in the structure of the solvation shell. This shell consists of water molecules, because the IR spectrum of the thin film is similar to the vibrational spectrum of liquid water [25] in the range 3150–3600 cm^{-1} (Fig. 3, inset, curve 2). In contrast, the intensity of the absorption band in the same region of the IR spectrum of the thin film with a charge transfer complex decreases considerably and the band becomes narrow. This evidence suggests dramatic changes in the structure of the solvation shell (curve 1). This result agrees with the data of resonance Raman light scattering, which indicate changes in the solvation shell in associated porphyrin solutions as a result of the formation of a donor–acceptor complex [12].

The presence of minor amounts of water in thin films of associated Porphyrin II also changes the structure of the UV spectrum (Fig. 4, curve 1). The UV spectrum shows a new band in the 670–900 nm region, the maximum of which is shifted by 40 nm as compared with the charge transfer band in Porphyrin III thin films. Appreciable absorption in about the same spectral region but at $\lambda_{max} \approx 750$ nm is built up after hydration of the thin film (Fig. 6, curve 3). This may be connected with a change in the vibrational dynamics of associated porphyrin molecules as a result of replacing some DMF molecules by water. Examination of the IR spectra of Porphyrin III and Porphyrin II films shows that the structure of

the solvation shell of associated Porphyrin II is quite different from that of associated Porphyrin III. Drying of Porphyrin II (Fig. 8) shows that amino groups are hydrated even in the solid state, since their absorption in the region of deformational and valence vibrations is higher than that of dried porphyrin (compare curves 2 and 3 with curve 1). Also, dehydration results in the appearance of the 1593 cm^{-1} band, which is likely to be related to the deformational vibrations of phenyl rings. At the same time, hydration leads to a redistribution in intensity of the bands in the range 1370–1450 cm^{-1}, which is likely to be related to some changes in the solvation shell upon interaction with water molecules.

The peculiarities in the IR spectra of Porphyrin II films at 2800–3600 cm^{-1} are related to a strong intermolecular interaction between solvated porphyrin molecules. The 1667 cm^{-1} band of DMF vibrations in the IR spectrum of the thin film also suggests the presence of a local solvation shell around the associated porphyrin (Fig. 6, inset, curve 1). The shoulder at 1653 cm^{-1}, which is clearly visible in the region of deformational vibrations of water molecules, indicates that water is involved in the structure of the solvation shell in thin films prepared in the presence of minor amounts of water. Examination of curves 2 and 3 (Fig. 6, inset) as well as Fig. 2 (curve 3) and fig. 8 (curve 3) shows that the local solvation shell is preserved upon film hydration in spite of the fact that the band at 1667 cm^{-1} vanishes.

Note that the frequencies of solvated or hydrated amino groups practically do not shift as a result of solvation or hydration of Porphyrin II. However, the solvation results in a significant increase in the intensity of the absorption bands of deformational and valence symmetric vibrations as compared with asymmetric vibrations (Table 2). A similar effect probably occurs in the case of the presence of water in the porphyrin thin film. However, in this case the maximum at 1618 cm^{-1} (Fig. 4, curve 1 and Fig. 7, inset, curves 2 and 3), which leads to a considerable increase in relative intensity at this frequency, should be assigned to the deformational vibrations of water molecules.

The deformational vibrations of the molecules in liquid water ($\nu_2 = 1645$ cm^{-1}) are known to be characterized by a higher energy as compared with the vibrations of free water molecules ($\nu_2 = 1595$ cm^{-1}) [26]. At the same time the frequency of the water molecules (1653 cm^{-1}) involved in the structure of the solvation shell is close to the frequency of the deformational vibrations in the structure of ice ($\nu_2 = 1650$ cm^{-1}). The frequency (maximum at 1618 cm^{-1}) assigned to the deformational vibrations of water molecules has an intermediate value between those of volume and free molecules. Hence the water molecules associated with the maximum at 1618 cm^{-1} are not involved in the structure of the volume phase but form bridges between neighbouring molecules of associated porphyrin. The shift of the band of N–H vibrations of the pyrrole rings in Porphyrin II by 95 cm^{-1} towards the low frequency region (Table 1) and the increase in the band intensity in the thin film as compared with the solid state (Table 2) suggest the existence

of hydrogen bonds between neighbouring molecules in porphyrin. The presence of minor amounts of water results only in marked changes in the UV spectrum of the thin film. Therefore water molecules are involved in the structure of the donor–acceptor complex formed by associated molecules of Porphyrin II.

Marked changes in the intensity of the doublet bands, i.e. the bands at 1473 and 1440 cm^{-1} associated with the C=N and C–C vibrations of the porphyrin macrocycle [17,27], as well as the shift of the bands of the C–H groups in the low frequency region indicate a considerable redistribution of electronic density in conjugated bonds of Porphyrin II. A well-pronounced IR band at 1285 cm^{-1} of Porphyrin II suggests the presence of sufficient amounts of porphyrin radical cations formed as a result of the interaction with oxygen molecules. However, the quantity of superoxide radicals, as evidenced by the IR band at 1060 cm^{-1}, is lower than that expected. Unfortunately, we could not elucidate the light or dark process which leads to the formation of the donor–acceptor complex and consequently to the superoxide radical formation. The procedure of film preparation requires visual control. However, if the process is a photochemical act, then in this case it has a high light sensitivity. From this point of view, the low quantity of superoxide radicals registered in the solid state of Porphyrin II might be due to their formation only in the surface layer of the aggregates under light action. On the other hand, the frequency of the vibrations of the superoxide radical may experience changes upon hydration. Evidently the presence of water molecules provides the only condition for the interaction of porphyrin with oxygen molecules, i.e. a certain humidity of air.

Hence the presence of minor amounts of water in the solvent is necessary for the formation of the intermolecular complex. Realization of the donor–acceptor interaction in the complex between neighbouring molecules of associated porphyrin is allowed owing to the direct involvement of water molecules forming bridges of hydrogen bonds in the complex structure. The formation of intermolecular bridges results in charge delocalization in the π system of the complex composed of associated porphyrin molecules when the structure of the complex is stabilized by the solvation shell. As a result, a new electronic transition occurs at a lower excited state as compared with the $Q_x(0–0)$ transition of associated Porphyrin II.

5. Conclusions

The data of IR spectroscopy show that strong solvation takes place in Porphyrin II associated in thin films. The formation of the solvation shell around porphyrin is a result of the selective binding of solvent molecules by the most polarized atom groups. Such groups are the following: amino groups of phenyl rings and C–H, C=N and N–H groups of the porphyrin macrocycle. Dehydration of Porphyrin II in the solid state shows that porphyrin contains water traces under

normal conditions. Water does not form a volume phase but only bridges between molecules of associated porphyrin. With the presence of minor amounts of water in thin films of Porphyrin II, water participates in the formation of the solvation shell. At the same time, water molecules are involved in the donor–acceptor complex, forming bridges of hydrogen bonds. As a result of the interaction, stabilization of the vibrational state of the donor–acceptor complex between molecules of associated porphyrin takes place. The appearance of a new broad band in the red and near-IR region of the UV spectrum suggests the formation of a new low energy excited state of the complex in the presence of minor amounts of water in the thin film. The formation and stabilization of the intermolecular donor–acceptor complex are prevented when the water molecules in Porphyrin II thin film are replaced by an organic solvent.

The formation and stabilization of a donor–acceptor complex between associated molecules of Porphyrin III are also observed in the presence of water traces in the thin film. The results of IR spectroscopy show that the formation of the complex is accompanied by a change in the solvation shell. Note that the formation of the donor–acceptor complex is not allowed in the presence of compounds with stronger electron-donating (TEA) or electron-accepting (CCl_4) properties as compared with porphyrin. In contrast with Porphyrin III, the structure of the solvation shell in Porphyrin II remains unchanged upon formation of the donor–acceptor complex. At the same time, the interaction of oxygen molecules with Porphyrin II and the direct incorporation of water molecules into the structure of the donor–acceptor complex may provide the basis for further development of a model chemical system which is capable of simulating photoinduced water decomposition to yield hydrogen and oxygen.

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