the distal site in a hemoprotein.

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Registry No. Meso-Rh(III), 86863-10-7; Deut-Rh(III), 86863-11-8; Meso-CH_3-Rh(III), 86863-12-9; MesoDME, 1263-63-4; $[Rh(CO)_2Cl]_2$, 14523-22-9; MesoDME-Rh(III), 86863-13-0; DeutDME-Rh(III), 86884-69-7; MesoDME-CH_3-Rh(III), 86863-14-1.

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Complexation of Zinc Tetraphenylporphyrin by Adsorbed Poly(4-vinylpyridine): Equilibrium Studies

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We have measured equilibrium constants for the reversible complexation of zinc tetraphenylporphyrin with poly(4-vinylpyridine) both in solution and in a system in which the polymer had been adsorbed onto fused silica. The complexation of the porphyrin with adsorbed polymer follows the behavior expected for reversible complexation at independent sites (so-called Langmuir-type isotherm). The equilibrium constant for complexation to the polymer in solution is somewhat smaller than that for complexation to pyridine, but the equivalent quantity for complexation to the polymer adsorbed onto silica is very large.

Introduction

Porphyrin compounds have elicited considerable interest for a long time as potential sensitizers for photochemical and photoelectrochemical processes, in particular for processes involving energy storage.[1-7] Among these interests has been an interest in attaching porphyrin compounds to electrodes or to materials that might serve as electrodes.[8-14] One method of attachment available is the ligation of a metalloporphyrin through its axial position(s) to groups that are naturally found on a surface or that have been introduced onto a surface by chemical modification of the surface. In the work we report herein, we have measured the equilibrium properties of zinc tetraphenylporphyrin with poly(4-vinylpyridine), the latter in solution or as a surface modifier on fused silica. Poly(4-vinylpyridine) as a surface-modifying agent, especially for graphite electrodes, has been studied by Anson's group.[15-18] The polymer proves to adsorb to surfaces of many kinds and could, thus, serve as a modifying agent for various electrodes or as a part of a heterogeneous catalytic system.

Experimental Section

Zinc tetraphenylporphyrin (ZnTPP) was synthesized and purified by using the methods of Adler et al.[19] Poly(4-vinylpyridine) was purchased from Aldrich Chemical Co. Inc. and used as received. The product used is a 4-vinylpyridine/styrene copolymer with 10% styrene. It has a weight-average molecular weight, from viscosity, of 3.2×10^5. We abbreviate it henceforth as PVP. Spectral grade benzene was used without further purification. Pyridine and methylene chloride were purified by standard procedures.[20] The quartz substrates were flat rectangles with dimensions of 5.0 cm × 1.0 cm × 0.1 cm and were of Suprasil grade quartz.

Prior to exposure to PVP, the quartz flats were cleaned by boiling in dilute HNO_3 and rinsed thoroughly with deionized water. They were then rinsed heavily with CH_3OH and oven-dried for 1 h at 110 °C. Then the samples were cleaned with CH_2Cl_2 and placed into a 0.5% solution of PVP in CH_2Cl_2 for 30 min. Afterward the samples were rinsed with CH_2Cl_2 and analyzed. PVP samples were coordinated with ZnTPP by being placed into a fresh 10^{-3} M solution of ZnTPP in benzene for 1 h. The samples were rinsed with benzene, analyzed, and treated appropriately for further reaction.

All UV and vis spectra were recorded on a Varian Cary 219 spectrophotometer or a Perkin-Elmer 552 spectrophotometer. The PVP coverages were based on pyridine units as determined by the difference in absorption between 257 and 280 nm. The difference of the extinction coefficients was obtained from PVP in CH_2Cl_2 at the same wavelengths. This corrected for any background scattering due to surface roughness of the quartz substrates. The extinction

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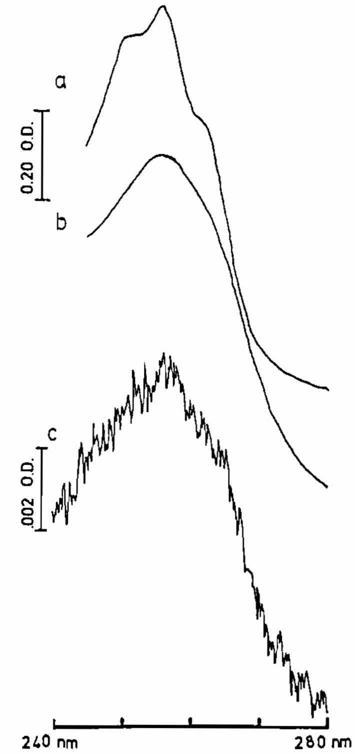

Figure 1. UV spectra of (a) pyridine in CH_2Cl_2, (b) PVP in CH_2Cl_2, and (c) PVP on quartz.

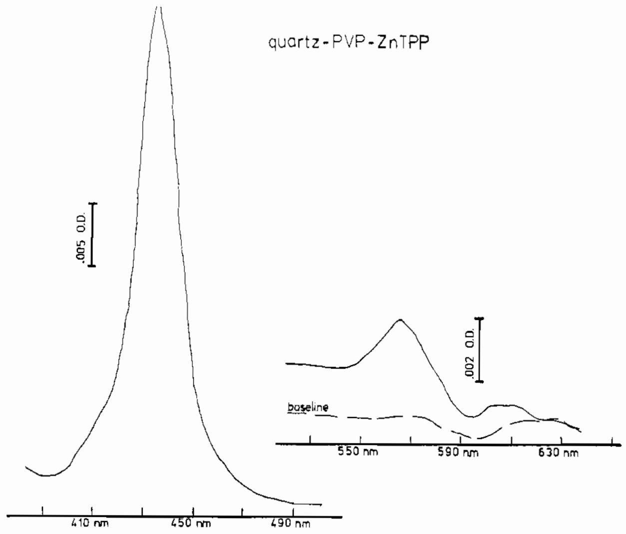

Figure 2. Visible spectrum of a quartz/PVP/ZnTPP sample.

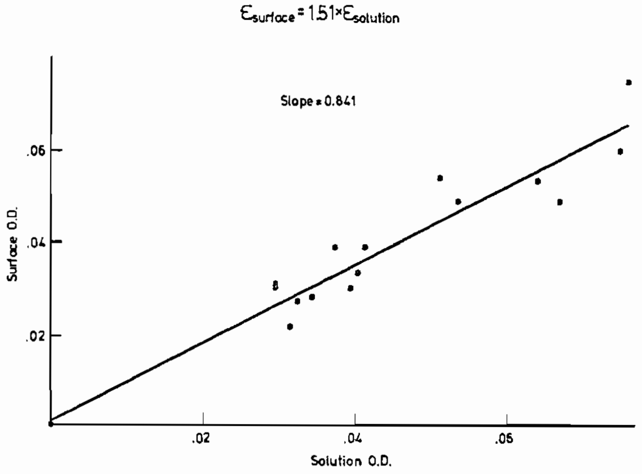

Figure 3. Plot of the surface OD of a quartz/PVP/ZnTPP sample vs. the OD of a solution for that sample whose ZnTPP was quantitatively removed into a CH_2Cl_2 solution of 0.12 M pyridine.

coefficient of ZnTPP on the surface was determined by measuring the intensity of the Soret band of the quartz/PVP/ZnTPP sample, removing the ZnTPP into a solution of 0.12 M pyridine in benzene, and measuring the Soret intensity of the pyridine–ZnTPP–benzene solution. It was found that solutions of pyridine removed ZnTPP quantitatively from surfaces modified with PVP. This procedure allowed us to obtain a surface extinction coefficient for the adsorbed ZnTPP.

The equilibrium constant of ZnTPP with PVP in solution was obtained by using the method of Miller and Dorough.[21] The equilibrium constant (K_{eq}) of ZnTPP with quartz/PVP was determined from a Langmuir-type expression for sufficiently high concentrations of solute[22]

$$\alpha^{-1} = \frac{k_2}{k_1\alpha_0}C^{-1} + \alpha_0^{-1} \qquad (1)$$

where $k_1/k_2 = K_{eq}$, C is the solution concentration of unbound ZnTPP in M, α is the concentration of surface-bound ZnTPP in mol cm^{-2}, and α_0 is the maximum value of α corresponding to the maximum number of surface sites that can be occupied by porphyrin molecules. Equilibrium concentrations of solution species (C) were determined from Beer's law, and the equilibrium areal concentrations of surface-bound material were determined by using the surface extinction coefficient, measured as described previously.

The equilibrium optical densities were determined by placing a quartz/PVP/ZnTPP sample into a 1-cm quartz cuvette fitted with an O-ring cap. To this was added 6 mL of benzene. The Soret region was scanned until no further change could be detected. The sample was then removed, and the optical densities of the solution and the sample were measured at their respective Soret energies. We had previously noted that immersion of a quartz/PVP/ZnTPP sample in benzene resulted in a rapid change of areal density of adsorbed porphyrin, over a period of less than 5 min, followed by no detectable further change.

Results

Figure 1 shows the UV spectra of pyridine and of PVP in solution. The extinction coefficient of PVP in CH_2Cl_2 at 257 nm was found to be 3.57×10^3 M^{-1} cm^{-1}, on the basis of the concentration of pyridyl groups. This value agrees well with those previously reported.[23,24] The difference in the extinction coefficient measured at 257 and 280 nm was found to be 3.03×10^3 M^{-1} cm^{-1}. The UV absorption spectrum of a quartz/PVP sample, shown in Figure 1, appears to be the same as that of PVP in solution. From the difference in extinction coefficients obtained, it was found that there was 0.089 pyridyl unit/Å^2 on 1.48×10^{-9} mol cm^{-2} of pyridyl units. On the basis of the average molecular weight of 3.2×10^5 reported above, one PVP polymer unit has some 2.99×10^3 pyridyl groups and thus occupies 3.36×10^4 Å^2 of surface.

Quartz/PVP/ZnTPP samples have visible absorption spectra (Figure 2) much like those of solution PVP·ZnTPP. Figure 3 shows a plot of the surface OD vs. the solution OD for samples from which surface-bound porphyrin was quantitatively removed into solution. The slope of 0.84 indicates the extinction coefficient of quartz/PVP/ZnTPP is 1.51 times greater than that of py·ZnTPP in benzene after taking into account the area of the samples and the volume of solution used, or 9.0×10^5 mol^{-1} cm^2. The samples had optical densities of 0.02–0.08. This is equivalent to 6.69×10^{-4} to 26.76×10^{-4} molecule of ZnTPP/Å^2 (1.11×10^{-11} to 4.44×10^{-11} mol cm^{-2})

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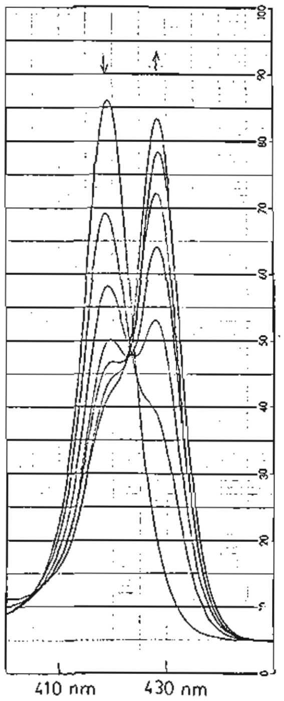

Figure 4. Visible spectra of the Soret region of 2.58×10^{-6} M ZnTPP in CH_2Cl_2 to which 10, 20, 30, 40, 50, and 60 μL of 0.049 M PVP (based on pyridine units) was added.

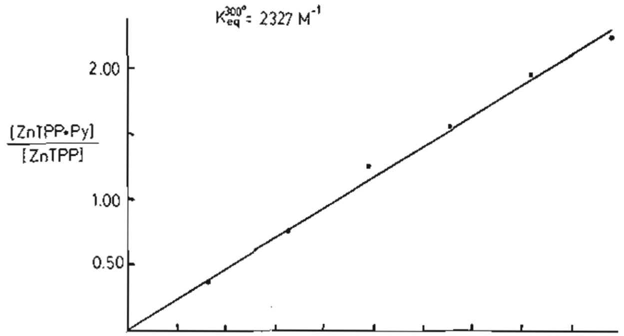

Figure 5. Equilibrium plot of [ZnTPP·py]/[ZnTPP] vs. [py] in CH_2Cl_2 where py is a pyridine unit present in the form of poly(4-vinylpyridine. The slope indicates $K_{eq} = 2327\ M^{-1}$.

or an area of 374 to 1495 Å^2/ZnTPP molecule.

Figure 4 shows the effect of adding PVP to a 2.58×10^{-6} M solution of ZnTPP in CH_2Cl_2. The plot in Figure 5 shows that the monopyridine complex is formed since the plot is linear. The equilibrium constant was found to be 2327 M^{-1}. This is lower than the values of 6900 M^{-1} for pyridine and ZnTPP reported by Valentine and Nappa[25] in CH_2Cl_2, which we confirmed.

Similar spectra were obtained when quartz/PVP/ZnTPP samples were placed into a cuvette of benzene (Figure 6). Figure 7 is a plot of the data obtained. All of the samples used had 0.089 pyridyl group/Å^2. The plot shows that the coordination of ZnTPP to the PVP-derivatized surface obeys Langmuir-type absorption and that only the monopyridine species was formed. The equilibrium constant (defined as k_1/k_2 in eq 1) was found to be $2.74 \times 10^8\ M^{-1}$. This quantity is directly comparable to the solution equilibrium constant. It represents the inverse of the equilibrium ZnTPP concentration in solution needed to achieve complexation of half the surface-immobilized pyridyl groups, as the solution equilibrium constant represents the inverse of [ZnTPP] needed to complex half the pyridine. This value is substantially larger than the values of 5300[26] and 6030 M^{-1} [27] reported for pyridine and ZnTPP in benzene. The value of α_0, which corresponds to the number of surface sites to which ZnTPP can coordinate, is found to be 5.68×10^{-11} mol cm^{-2}, or 3.42×10^{-3} molecule of ZnTPP/Å^2 or 293 Å^2/molecule of ZnTPP.

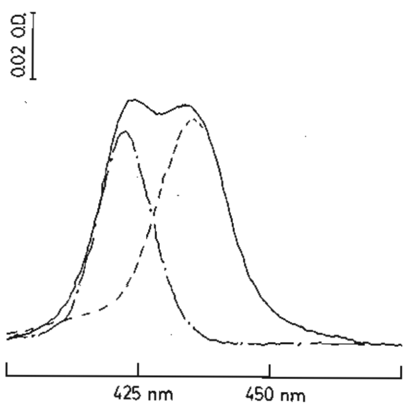

Figure 6. Visible spectra of (—) a quartz/PVP/ZnTPP sample placed into a cuvette of benzene, (–•–) the solution after the quartz/PVP/ZnTPP sample was removed, and (—) the resultant quartz/PVP/ZnTPP sample placed into an empty cuvette.

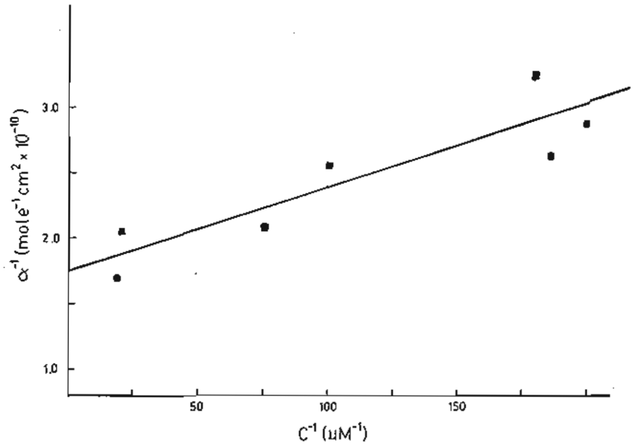

Figure 7. Langmuir-type plot for the equilibrium concentrations of quartz/PVP/ZnTPP as a function of C (solution concentration of ZnTPP). The slope indicates $K_{eq} = 2.74 \times 10^8\ M^{-1}$.

Discussion

There are four salient features in our results. One feature is qualitative. We can fit our observations on the adsorption of ZnTPP to PVP-modified silica surfaces with a model in which reversible absorption is assumed.

The extinction coefficient of adsorbed ZnTPP is shown to be 1.51 times that of the same species (ZnTPP·py) in solution. The most obvious interpretation of this observation is that there is a strong preferential orientation of the ZnTPP plane parallel to the surface of the silica. Since the absorption spectrum is polarized in the molecular plane, such an orientation would yield an extinction coefficient of three-halves that of a randomly oriented sample. Our results do not, of course, prove this interpretation. There could be, for instance, a hypsochromic shift in the spectrum due, for instance, to conformational changes of the molecule on the surface. The interpretation we suggest can only be proven by measuring spectra away from the normal incidence. We are currently engaged

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in preparing for such measurements.

The major results of the study are, of course, the two binding constants. These are not exactly comparable to the binding constants between ZnTPP and pyridine, but certain features are clear. The numbers quoted (2327 M^{-1} for ZnTPP binding to PVP in CH_2Cl_2 and 2.74×10^8 M^{-1} for ZnTPP binding to PVP on silica from benzene solution) are limiting binding constants that avoid any concern with steric interactions among the ZnTPP molecules. This is because the measurement on solution PVP was made at such low concentrations of ZnTPP that a given polymer had, on the average, less than one bound ZnTPP and because the model used for surface adsorption considered explicitly the limited number of adsorption sites available.

The result obtained with PVP in solution is expected. CH_2Cl_2 is only a moderately good solvent for PVP; the polymer is somewhat contracted and, thus, not all the pyridyl groupings are available for adsorption. This, added to any steric repulsion between the ZnTPP and portions of the polymer to which the molecule is not bonded, makes the fall in binding constant understandable.

The very large binding constant of ZnTPP to the modified surface is harder to understand. Poly(4-vinylpyridine) is believed to adsorb to a surface with only a few segments of the molecule in intimate contact with the surface. The rest of the molecule is essentially free and extends out into the solution, assuming a structure similar to the structure a molecule has in solution.[28,29] This suggestion is based on the observation that a large fraction of the pyridyl groups are available for reaction in the adsorbed system. This observation applies to our system, the polymer adsorbed onto a silica surface, as well as to the system for which it was originally made, PVP adsorbed onto graphite.

Our observations show that the model needs modification to deal with the reaction of ZnTPP with the adsorbed polymer. First, the equilibrium constants yield a $\Delta G°$ of transfer of ZnTPP from pyridine in solution to a pyridyl of the adsorbed polymer of -6393 cal mol^{-1}. $\Delta G°$ of transfer from pyridine to a pyridyl of the polymer in solution is much smaller and is of the opposite sign, $\Delta G° = +201$ cal mol^{-1} (in CH_2Cl_2). Second, the molar extinction coefficient of ZnTPP absorbed on the modified surface is not the same as that of the pyridine complex in solution. As mentioned above, easily the most obvious explanation of the change in molar extinction coefficient is that the ZnTPP is oriented by the surface.

Some of the effects we see must be due to the size of the porphyrin molecule, which is not small compared with other dimensions in the system. The porphyrin molecules are 14 Å on a side, in the sense that a square drawn around its plane would need to have such a length. A polymer film having the density of the solid would only be 10 Å thick to provide the observed area density of the pyridyl groupings. The strong preferential orientation of the porphyrin is, thus, not expected.

It is not possible to discuss the thermodynamic aspects of the adsorption of the ZnTPP without a more detailed model of the modified surface. It seems more likely, however, that some degree of organization of the PVP by the surface is responsible for these effects as well.

Conclusions

Zinc tetraphenylporphyrin is found to adsorb reversibly onto silica surfaces modified with poly(4-vinylpyridine). The adsorption obeys a simple isotherm, but the thermodynamics of adsorption is quite different from that of binding to a polymer in solution, with the effect of making adsorption very efficient. These results will perhaps be helpful to those who wish to use porphyrin compounds in interfacial systems, perhaps as sensitizers.

Registry No. Zinc tetraphenylporphyrin, 14074-80-7; poly(4-vinylpyridine) (homopolymer), 25232-41-1; vitreous silica, 60676-86-0.

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Protonation and Aquation of Chromium(III)/Ethanolamine Complexes in Aqueous Solution

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Several Cr(III) complexes with amino alcohols have been prepared, and the solution chemistry of the tris(2-aminoethanol) complex has been studied in detail. Addition of excess strong acid to solutions containing $Cr(Eta)_3^0$ (Eta = bidentate aminoalkoxy) results in the following sequence of reactions: stage I, instantaneous protonation to produce bidentate $Cr(EtaH)_3^{3+}$ (EtaH = 2-aminoethanol); stage II, rapid (complete in ~10 min at 20 °C) conversion to monodentate $Cr(EtaH)_3(OH_2)_3^{3+}$ by ring opening at the alcohol function; stage III, slower stepwise aquation of the N-bonded ethanolamine to produce $Cr(OH_2)_6^{3+}$. The first-order rate constants in stage III (25 °C, $\mu = 0.10$) are $k_{3\to 2} = 2.3 \times 10^{-4}$ s^{-1}, $k_{2\to 1} = 1.7 \times 10^{-5}$ s^{-1}, and $k_{1\to 0} = 6.4 \times 10^{-7}$ s^{-1}. Aquation rates in stages II and III ($k_{1\to 0}$) are much faster than normal for Cr(III) complexes but have a precedent in the Cr(III)/ethylene glycol system.

Introduction

With the exception of the amino acids, there has been relatively little study of bidentate ligand complexes containing one nitrogen and one oxygen donor. There has also been relatively little reported on complexes containing ligands with alcohol functional groups as binding sites, probably because the oxygen atoms are usually poor donor atoms.

Some earlier work[1-5] on ethanolamine complexes of Cr(III) was largely preparative in nature and did not provide a con-

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