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A Simple Method for the Determination of pK_3 Value of Porphyrins

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To determine the pK_3 value of porphyrins, a simple spectrofluorometric titration method has been developed. The porphyrin solution is titrated with perchloric acid. After each addition of acid, the porphyrin solution is excited at one suitable wave length and the emission intensity is measured at another suitable wave length. The pK_3 values of twelve porphyrins have been determined. Nitrobenzene, toluene and water have been used as solvents. The pK_3 values have been compared with the literature values. Attempt has been made to correlate the Cu^{+2} insertion kinetics of six porphyrins and their pK_3 values.

The proton dissociation equilibria of a porphyrin is given by 1)

$$PH_4^{2+} \underset{H+}{\overset{pK_4}{\rightleftharpoons}} PH_3^{+} \underset{H+}{\overset{pK_3}{\rightleftharpoons}} PH_2 \underset{H+}{\overset{pK_2}{\rightleftharpoons}} PH^{-} \underset{H+}{\overset{pK_1}{\rightleftharpoons}} p^{2-}$$

where the PH_2 is the free base porphyrin and PH_4^{2+}, PH_3^{+}, PH^{-}, and p^2 are respectively the dication, monocation, monoanion and dianion species of the PH_2. pK_3 values of porphyrins have been found to be more sensitive to substituent effects than pK_4 and correlated to a number of aspects of porphyrin coordination chemistry. 2) Titrating absorption spectroscopically in nitrobenzene solution with perchloric acid ($HClO_4$), Aronoff 3) grouped porphyrins into three types; porphyrins showing (1) distinct PH_3^+, (2) indistinct PH_3^+ and (3) indistinguishable PH_3^+. The majority of the naturally occurring porphyrins, as well as 5, 10, 15, 20 - substituted porphyrins fall in the second type, where the pK_3 and pK_4 are very close. Absorption spectroscopic technique relies upon the molar absorptivity value of PH_3^+ at certain wave length and it is difficult to determine this value accurately for porphyrins with indistinct PH_3^+. Therefore, this method can only be useful to obtain an estimate of pK_3.

In this work, we report a simple emission spectroscopic titration method to determine the pK_3 value of porphyrins in general. In this method, advantage is taken of the fact that only free base porphyrins (PH_2), and not its PH_3^+ and PH_4^{2+} forms, show fluorescence emission properties. In actual experiment, a $HClO_4$ solution in dioxane, for nonaqueous titration, is prepared according

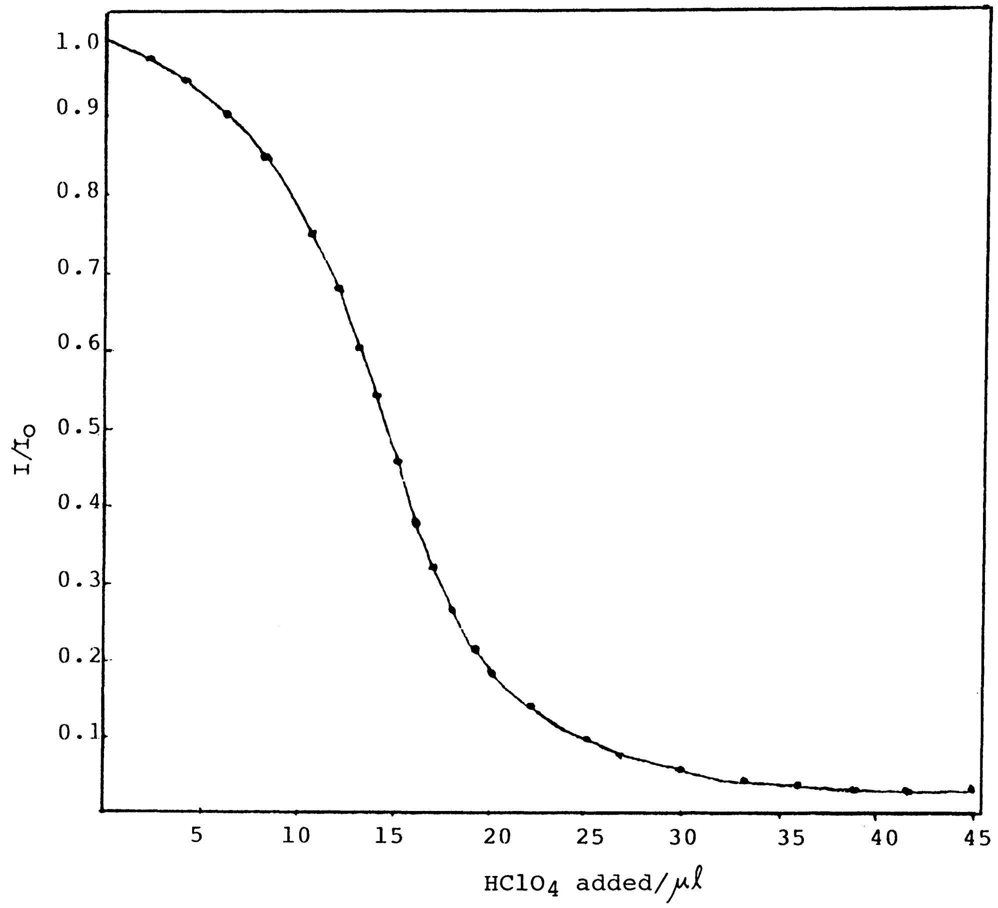

Fig. 1. Titration curve for porphyrin VI (2×10^{-6}M) in nitrobenzene with $HClO_4$ (7.8×10^{-2}M in dioxane). I/Io is corrected for dilution. λex and λem are 519 and 629 nm respectively.

to Aronoff [3]; for aqueous titration, water replaces dioxane. The porphyrin is dissolved in a suitable and carefully purified solvent (nitrobenzene, toluene and water) at a micromolar concentration. A 2.5 ml porphyrin solution, taken in a fluorescence cell, is titrated with 1 aliquots of $HClO_4$ and the fluorescence emission intensity (I) is measured each acid addition. For reference emission intensity (I_o), the same porphyrin solution and the same volume of solvent used in preparing the $HClO_4$ solution, are used. For most of our experiments, λex and λem were around 519 nm and 659 nm respectively. Any suitable pair λex and λem can be used. In this study an SLM 4800S Spectrofluorometer and an SLM/AMINCO DW2R UV-visible spectrophotometer were used. All titrations were carried out at 25± 0.1 °C maintained with a circulating water bath and thorough mixing was assured by magnetic stirring.

In Fig. 1, a plot of 1 of $HClO_4$ vs. corrected I/Io for porphyrin VI in nitrobenzene, shows a typical titration curve. If the titrations, as outlined above, are monitored by recording absorption spectras (560-700 nm), following the addition of $HClO_4$, an isosbestic point is observed between 550 and 560 nm, indicating the presence of the two species, PH_2 and PH_3^+. This isosbestic

Table 1. pK_3 values of porphyrins

	Porphyrin	Solvent	pK_3 ±.01	Rate of Cu^{+2} insertion in DMF solution (min^{-1})4)	Reference
1.	5,10,15,20-Tetraphenylporphine	Nitrobenzene	3.99	0.2229	This work
		Nitrobenzene	4.38	-	3
2.	5,10,15-Triphenyl-20-[4-(benzyloxy)-phenyl]porphine 4)	Nitrobenzene	4.14	0.2663	This work
3.	5,15-Diphenyl-10,20-bis [4-(benzyloxy)phenyl]-porphine 4)	Nitrobenzene	4.19	0.3816	This work
4.	5,10-Diphenyl 10,20-bis[4-(benzyloxy) phenyl]porphine 4)	Nitrobenze	4.21	0.4963	This work
5.	5-Phenyl-10,15,20-tris[4-benzyloxy)-phenyl]porphine 4)	Nitrobenzene	4.24	0.6518	This work
6.	5,10,15,20-Tetrakis [4-(benzyloxy)-phenyl]porphine	Nitrobenzene	4.28	0.6001	This work
7.	21-Methyltetraphenylporphine 6)	Toluene	5.82		This work
		Nitrobenzene	5.64		9
8.	4 TMPyP 7)	Water	3.38		This work
9.	3 TMPyP 7)	Water	3.66		This work
10.	2 TMPyP 7)	Water	3.77		This work
11.	Tetrakis[p-(trimethylammonio)-phenyl]porphine 7)	Water	2.92		This work
12.	5,10,15,20-Tetrakis[p-(ethyl-methylsulfonis)phenyl]-posphyrin tetraperchlorate	Water	2.73		This work

point persists until the I/Io value reaches around 0.3. Thus, the pK_3 value can be easily calculated from the titration curve.

Table 1 shows the pK_3 values of a number of porphyrins, seven water-insoluble and five water-soluble. Except for N-methyltetraphenylporphyrin 7, nitrobenzene was used as a solvent for the water-insoluble porphyrins. In this solvent VII exhibited molecular interaction, monitored by absorption spectroscopy, similar to that reported by Guilleux, et al. 9) However, the reported pK_3 value of 7 in nitrobenzene is comparable to our value in toluene (see Table 1), the estimated pK_3 value of tetraphenylporphyrin, reported in the literature [1)] is also comparable to that obtained by our method. To our knowledge, no one has published the pK_3 values for the water-soluble tetracationic porphyrins reported here. The pK_3 values suggest that these water soluble porphyrins (VIII through XII) are weaker bases, compared to the porphyrins containing polyanions. [1)] The pK_3 values of 4TMPyP, 3TMPyP and 2 TMPyP, also indicate that the electron withdrawing effect of each of the <u>meso</u> substituents is primarily operating through inductive effect, and not by resonance effect. Since a sulfonium group is expected to be a stronger electron withdrawing group than a trimethylammonium ion, porphyrin XII should be less basic than XI, and their pK_3 values prove that.

A benzyloxy group, like a methoxy group, will be electron withdrawing inductively. The decreasing pK_3 values in porphyrins I through VI, where the benzyloxy groups are added to the <u>para</u> position of phenyl rings, indicate that this group is withdrawing electrous inductively. The rate of Cu^{+2} insertion in DMF solution for porphyrins I through VI were carried out using procedure described elsewhere. [4)] The kinetic data, except for VI, are consistent with the pK_3 values. It appears, that properties other than the pK_3 values of porphyrins may play important roles in Cu^{+2} insertion kinetics in DMF. [2)]

To summarize, a simple and accurate spectrofluorometric titration method for the pK_3 value of porphyrins, at a concentration allowing them to remain as a monomer, has been developed. This method should lend itself the determination of pK_3 value of porphyrins in any solvent or combination of solvents using any suitable acid.

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