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Thin-Layer Chromatography of Tetraphenylporphin and Its Metal Complexes

Mitsuo Sato and Takao Kwan

Faculty of Pharmaceutical Sciences, The University of Tokyo[1]

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Petroleum crudes contain metal porphyrins which are known to poison catalysts when the petroleum is subjected to a catalytic hydrodesulfurization. During the course of our hydrodesulfurization studies,[2-4] some preliminary investigations on the chromatographic separation of metal porphyrins were carried out, leading us to consider that a thin-layer chromatographic separation is superior and less time-consuming as compared with the paper chromatographic method.[5] In the present note we shall report such a thin-layer chromatographic method with respect to the separation of synthetic tetraphenylporphin and its metal complexes.

Experimental

Materials——Tetraphenylporphin (abbreviated to H_2TPP) and its vanadyl, nickel and copper complexes (abbreviated to VOTPP, NiTPP and CuTPP) were synthesized according to the usual manner,[6] and purified by recrystallization from benzene solutions.

Chromatographic Procedure——Glass chromatoplates (5×10 cm) were coated with a 250 μ layer of Silica gel G (Merck) and of Alumina G (Merck) and activated at 110—120° for two hours. Chloroform solutions of test substances were spotted along a line 2.0 cm from the lower end of the plates and developed by the ascending method. The run was stopped within 7 minutes, when the solvent had risen 7.0 cm beyond the original spots, and each spot was detected from its own colour.

The developing solvent systems utilized in this work were toluene–hexane mixtures of varying compositions (Table I).

Result and Discussion

The *Rf* values for H_2TPP, VOTPP and CuTPP obtained on Al_2O_3 layer as well as on SiO_2 layer with six developing solvents of toluene–hexane mixtures with varying compositions are given in Table I.

It was found that the *Rf* value for each sample decreased on both layers with increase in hexane contents of solvents, while the following sequence of *Rf* values was kept unchanged.

$$\mathrm{VOTPP} < \mathrm{H_2TPP} < \mathrm{NiTPP} - \mathrm{CuTPP}$$

A good separation was obtained on both layers for H_2TPP, VOTPP and NiTPP without any trailing as is illustrated in Fig. 1, and the degree of sample resolution which was calculated as the difference in the *Rf* values between VOTPP and NiTPP reached a maximum at about 30 v/v% hexane in the developer mixtures on the Al_2O_3 layer and at about 50 v/v% hexane on the SiO_2 layer.

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Table I. *Rf* Values for Tetraphenylporphin and its Metal Complexes

Layers	Complexes	Solvents[a)					
		S_1	S_2	S_3	S_4	S_5	S_6
Silica gel G	H_2TPP	0.87	0.75	0.58	0.36	0.11	0
	VOTPP	0.68	0.47	0.28	0.11	0.02	0
	NiTPP	0.93	0.85	0.72	0.62	0.43	0.02
	CuTPP	0.93	0.87	0.74	0.65	0.46	0.02
Aluminum oxide G	H_2TPP	0.85	0.81	0.76	0.62	0.32	0.01
	VOTPP	0.74	0.70	0.57	0.28	0.07	0
	NiTPP	0.88	0.86	0.83	0.80	0.71	0.19
	CuTPP	0.89	0.87	0.84	0.82	0.74	0.21

a) S_1: toluene, S_2: toluene-hexane (90-10), S_3: toluene-hexane (70-30), S_4: toluene-hexane (50-50), S_5: toluene-hexane (30-70), S_6: hexane

However, the separation of NiTPP from CuTPP did not take place even in the condition of a maximum resolution, although the *Rf* value for NiTPP seemed to be somewhat smaller than that for CuTPP.

On the other hand, the *Rf* value can be related to the adsorption coefficient (*K*) of a sample under the condition of a sufficiently low sample concentration by the Martin equation

$$Rf = 1/(1 + W/V \cdot K)$$

where *W* and *V* refer to the weight of adsorbent and the free volume accessible to solvent per unit area of thin-layer, respectively. Since W/V is kept constant for the same adsorbent and solvent system, the adsorbability of a sample as revealed by the magnitude of *K* can be compared with that of another sample directly from $(1\text{-}Rf)/Rf$ which is proportional to *K*.

Applying the above relation to the observed *Rf* values for our samples, it was found that the adsorbability decreased with the following sequence on both Al_2O_3 and SiO_2.

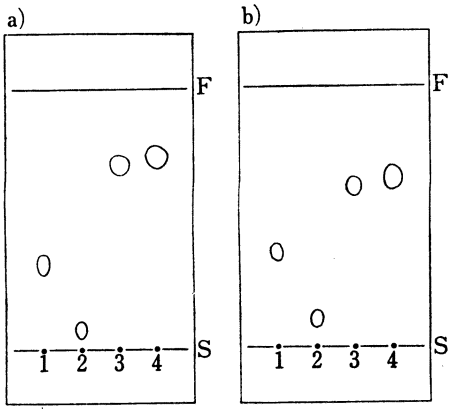

Figure caption

Fig. 1. Thin-layer Chromatograms for Tetraphenylporphin and its Metal Complexes

1. H_2TPP 2. VOTPP 3. NiTPP 4. CuTPP
a) adsorbent: aluminum oxide G (Merck)
solvent: toluene-hexane (30-70)
b) adsorbent: Silica gel G (Merck)
solvent: toluene-hexane (50-50)

$$\text{VOTPP} > H_2\text{TPP} > \text{NiTPP} - \text{CuTPP}$$

The greater adsorbability of VOTPP and H_2TPP as compared with that of NiTPP and CuTPP can be interpreted as due to the strongly polar sites in the former molecules, that is, vanadyl oxygen in VOTPP and N-H groups of the pyrrole rings in H_2TPP.

The above sequence is of interest in connection with the distribution of the metal porphyrins inside the hydrodesulfurization catalyst during the desulfurization reactions. It has been shown[2-4] that organic vanadium compounds in petroleum crudes are less diffusible than nickel compounds.

Our hydrodesulfurization catalysts have in fact contained silica and alumina as the support, and the distribution pattern for the two metal complexes inside the catalyst seems to be in harmony with the adsorbability sequence found in the present work.