Prediction of the Octanol/Water Partition Coefficients of Petroporphyrin Model Compounds

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The octanol/water partition coefficients (P_{OW}) were predicted for five vanadium(IV)–porphyrin complexes which were taken as model compounds of petroporphyrin. The correlation between the reversed-phase liquid chromatographic retention factor and the P_{OW} observed for standards was applied to the prediction. The $\log P_{OW}$ values estimated for the metalloporphyrins range from 5.8 (for 5,10,15,20-tetramethylporphine complex) to 10.1 (for 2,3,7,8,12,13,17,18-octaethylporphine complex).

The pollution of the sea and the lake due to the oil spillae, e.g., tanker accidents or pipeline brakes, is one of the serious environmental problems today. A micro amount of metallic eglement is included in petroleum, and vanadium is the metal of the most contents (10–100 ppm) in a lot of crude oil. It has been supposed that considerable portion of the vanadium are present in the forms of porphyrin complex that is so-called "petroporphyrin."[1] The vanadium petroporphyrin can be resolved into more than 20 species and the distribution of the species depends on oil.[2] Almost no discussion has been developed about the transfer of petroporphyrins in the environment, e.g., about bioconcentration, so far.

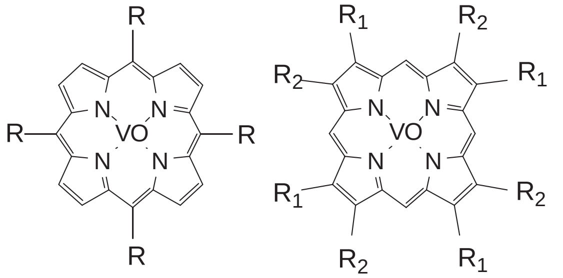
The *n*-octanol/water partition coefficient, P_{OW}, is one of the widely used physicochemical properties for measuring the hydrophobicity of chemicals and often used to estimate the extent of bioconcentration.[3,4] The methods for determining the P_{OW} values are classified into three main types. First is the direct measurement, such as, the shake flask method (SFM), the slow stirring method (SSM), and the generator column method.[5,6] The direct methods determine the quantity of the chemical of interest in both the water phase and the *n*-octanol phase. Second is the indirect method estimated from relationship between the P_{OW} and some physical properties, e.g., the water solubility or the retention factor on HPLC.[5,7] Third is the theoretical calculation, which utilizes empirical data.[8] The direct methods are the most reliable and recommended by OECD.[9] However, these traditional methods are time consuming and tedious, and require relatively large amounts of pure compounds. Besides, the difficulty in applying the direct methods increases with an increase in the hydrophobicity of test compound, e.g., in such a case as $\log P_{OW} > 6$, owing to technical difficulty in experiment.

The HPLC method uses the following relationship between the partition coefficient, P_{OW}, and the retention factor k' on HPLC:

$$\log P_{OW} = a \log k' + b, \qquad (1)$$

where a and b are empirical constants.[10]

The HPLC method is recommended by OECD test procedure, as well as SSM and SFM.[11] The HPLC method has been applied for many chemical compounds because it does not require long analytical time and any quantification of concentrations.



1a–1b **2a–2c**

1a: R = CH_3
1b: R = C_6H_5

2a: $R_1 = R_2 = CH_3$
2b: $R_1 = CH_3$, $R_2 = C_2H_5$
2c: $R_1 = R_2 = C_2H_5$

Chart 1.

The objective of this work is to get, for the first time, the approximate prediction of the P_{OW} values for five synthetic vanadium porphyrins (Chart 1) that are taken as model compounds of the petroporphyrin.

Porphyrin complexes of vanadium(IV) oxide **1a**, **1b**, and **2a** were prepared according to the general method reported by Adler et al.[12] Metalloporphyrins **2b** and **2c** were obtained commercially from Aldrich Chemical Co.

It is generally desirable for the HPLC methods that the compounds used as the standards are of high similarity as much as possible to the test compounds. But, there is actually no suitable compound that is structurally related to the petroporphyrin and also is of the property with $\log P_{OW} > 6$. Accordingly, 18 aromatic compounds whose $\log P_{OW}$ values had been known were used in this work, as the standards for predicting the $\log P_{OW}$ values of the metalloporphyrins.

A Shimadzu Model LC-10 HPLC system was equipped with an SPD-M10A photodiode-array detector. The separation column used was of typical ODS-type (Mightysil RP-18 GP, 5 μm, 4.6 mm i.d. × 150 mm, Kanto Chemical) with a guard column (Lichrosorb 100 RP-18, 4 mm i.d. × 4 mm, Merck). Chromatography was run in isocratic elution mode with a mixture of methanol and water (90/10, v/v) at a flow rate 1.0 $cm^3\,min^{-1}$, in a room regulated at a temperature 25 °C.

The retention factor (k') of a test compound was obtained from the equation

$$k' = (t_r - t_0)/t_0, \qquad (2)$$

where t_r is the retention time of the compound and t_0 is the mobile phase hold-up time in the column used. In this work, t_0 was determined from the retention time of uracil that was regarded to be unretained in the column. The measurements of t_r was carried out for every compound at least in triplicate, and relative

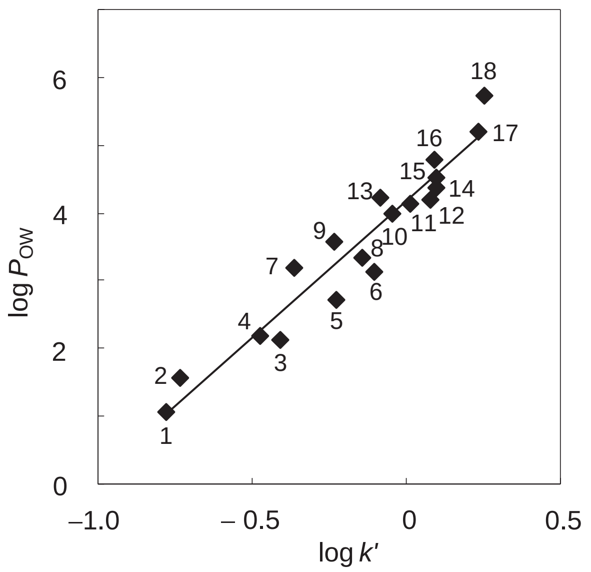


Figure 1. Plot of $\log P_{OW}$ versus $\log k'$ on reversed-phase HPLC. Compounds: 1, benzylmethanol; 2, phenylacetonitrile; 3, benzene, 4, propiophenone; 5, toluene; 6, *o*-xylene; 7, benzophenone; 8, naphthalene; 9, 9-fluorenone; 10, biphenyl; 11, diphenylmethane; 12, fluorine; 13, diphenyl ether; 14, dibenzotiophene; 15, phenanthrene; 16, 1,2-diphenylethane; 17, fluoranthene; 18, triphenylamine. The $\log P_{OW}$ values are cited from Ref. 5.

standard deviation was smaller than 3%.

The $\log P_{OW}$ versus $\log k'$ plot obtained for the standards used in this work is shown in Figure 1. One can find a correlation between $\log P_{OW}$ and $\log k'$; the regression line is given as

$$\log P_{OW} = 4.02 \log k' + 4.17\ (r^2 = 0.926,\ n = 18). \quad (3)$$

When the water content of the mobile phase was enlarged, higher correlation could be obtained, but the difficulty increased in determining the k' values of hydrophobic metalloporphyrins owing to remarkable increse in their retention time.

The $\log P_{OW}$ values of the petroporphyrin model compounds were predicted by applying the $\log k'$ values obtained for respective compounds to eq 3. The results are given in Table 1.

It is found that the $\log P_{OW}$ value tends to increase with an increase in the molecular weight of vanadiumporphyrin.

According to the $\log P_{OW}$ values obtained in this work, it is implied that petroporphyrins are considerably hydrophobic and possibility of bioconcentration in the environment should be taken into account. It is noted here that the $\log P_{OW}$ values estimated for most of the petroporphyrin model compounds are larger than those of dioxin and PCB; e.g., 6.42 for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin[13] and 7.13 for 3,3′,4,4′,5-pentachlorobiphenyl.[14]

Table 1. The P_{OW} values predicted for petroporphyrin model compounds at 25 °C

Entry	MW	$\log P_{OW}$
1a	431.38	5.8
1b	679.66	9.2
2a	487.49	8.4
2b	543.60	9.2
2c	599.70	10.1

It is still difficult, today, to determine the $\log P_{OW}$ values of hydrophobic vanadium(IV)–porphyrin complexes by calculation methods, because there are few partition data effective for compensative calculations. Although the $\log P_{OW}$ values predicted in this work are specified not to real petroporphyrins but to model compounds, the approximate P_{OW} values are expected to be useful at this stage for discussing the hydrophobicity and bioconcentration of petroporphyrins.

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