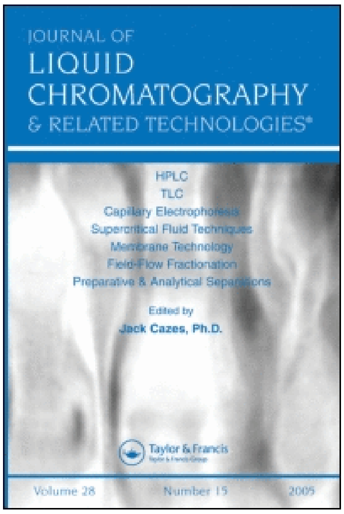

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S. K. Sahu[a]; G. G. Pandit[a]
[a] Environmental Assessment Division, Bhabha Atomic Research Center, Mumbai-85, India

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Estimation of Octanol-Water Partition Coefficients for Polycylic Aromatic Hydrocarbons Using Reverse-Phase HPLC

S. K. Sahu and G. G. Pandit*

Environmental Assessment Division, Bhabha Atomic
Research Center, Trombay, India

ABSTRACT

Retention time measurements on reverse phase HPLC columns at isocratic conditions are used to estimate the octanol-water partition coefficient for 16 polycyclic aromatic hydrocarbons (PAHs). The $\log K_{ow}$ values for PAHs ranged from 3.32 (napthalene) to 6.30 (Indeno(1,2,3-cd)pyrene). The estimated values obtained from the present study were in good agreement with the literature values. This is a simple and rapid method for simultaneous determination of octanol-water partition coefficients for different PAHs.

Key Words: Polycyclic aromatic hydrocarbons (PAHs); Partition coefficients; Octanol-water; RP-HPLC.

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*Correspondence: G. G. Pandit, Environmental Assessment Division, Bhabha Atomic Research Center, Trombay, Mumbai-85, India; E-mail: ggp@apsara.barc.ernet.in.

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INTRODUCTION

The octanol–water partition coefficient (K_{ow}) is a useful physiochemical property to model the fate and transport of organic pollutants in the aquatic and terrestrial environment. It has proved useful for predicting soil/sediment adsorption[1,2] and bioaccumulation factors for aquatic life.[3,4] The higher the value of K_{ow}, the greater the tendency of an organic pollutant to adsorb soil/sediment containing appreciable organic carbon, or to accumulate in biota.

In recent years, concern has grown about polycyclic aromatic hydrocarbons (PAHs) because many of these chemicals are considered to be carcinogenic.[5] PAHs are released into the environment through incomplete combustion of fossil fuels and remain there for a longer period.[6,7] Because of their persistence and toxic nature, it is important to model their behavior in the environment.

The traditional methods for determining the K_{ow} value are the shake flask[8] and generator column technique.[9] These methods are time consuming and require careful experimental techniques. A more rapid estimation of K_{ow} has been achieved using a regression equation between K_{ow} values of a compound with its retention capacity on reversed phase high performance liquid chromatographic (RP-HPLC) columns.[10–12] In this method, reference compounds with well-established K_{ow} values are chromatographed by RP-HPLC and their respective capacity factor (k') are determined. After a number of such compounds have been chromatographed, a calibration curve to be used for interpolation of $\log K_{ow}$ values for 16 PAHs is constructed by plotting $\log k'$ against $\log K_{ow}$. Although purely empirical, these RP-HPLC based methods have been proven useful and sufficiently reliable for many applications.[13] The indirect RP-HPLC determination of PAHs K_{ow} values in a mixture is attractive for several reasons. The method is rapid and clean, since emulsion formation and other phase contaminations do not occur. In addition, quantitation of the compounds in either phase is not necessary, since $\log K_{ow}$ determinations is only dependent on the compound retention time or a related parameter. The method is applicable to complex mixtures, so that many K_{ow} values can be determined in one experimental run. The present study contributes to the existing database on K_{ow} of polycyclic aromatic hydrocarbons and can also be used for modeling the fate and behavior of these chemicals in the environment.

EXPERIMENTAL

Reagents

The organic chemicals (benzene, *p*-xylene, toluene, ethylbenzene, 2,4,5-TCB, HCB, p,p'-DDT) used for the calibration curve were obtained from Merck. Individual and standard mixtures of sixteen compounds of PAHs were obtained from Supelco. Methanol, used as solvent for elution, was HPLC grade obtained from Spectrochem. All the chemicals were of the highest available commercial quality and were used for analysis without further purification.

Equipment

A Shimadzu model LC-10 high performance liquid chromatograph with manual injector (7125), SPD-10A UV-Vis detector, and a LC-10AD solvent pump was used for RP-HPLC. The column used was C-18 with 4 mm i.d. X 250 mm length and packed with 5 µm spherical particles. The integration of peak area was recorded by Chromatopac (C-R7A) data acquisition system.

Experimental Procedure

The calibration curve was constructed by injection of a known amount of reference compounds, such as benzene, *p*-xylene, toluene, ethylbenzene, 2,4,5-TCB, HCB, p,p'-DDT to provide at least 25% of scale deflection, while monitoring the UV spectra at 254 nm. The capacity factor (k') was determined for each compound by using the relationship, $k'\,(t_R - t_0)/\mathrm{t}_0$, where t_R and t_0 are the retention time of the compound and void volume, respectively. The t_0 value was obtained by measuring the retention time of formamide, which is not retained by the stationary phase of RP-HPLC. The organic compounds used for the calibration curve should have accurately known K_{ow} values; preferably by the shake flask or slow string methods. Between the $\log K_{ow}$ values of reference compounds and their respective capacity factor k', empirical relationships of the following type have been observed:

$$\log K_{ow} = A \log k' + \text{constant}$$

Therefore, the plot of $\log K_{ow}$ against $\log k'$ is a straight line with slope A.

The solvent used for the isocratic elution was 85% methanol and 15% water. The water was purified by the Milli-Q water purification system. This solvent was degassed before use by vacuum filtration. The flow rate through the RP-HPLC column was 1.0 mL/min. The temperature was relatively constant at 25°C. Individual PAH standards were injected at least thrice as described above, and their respective k' values were determined.

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Table 1. Data used to construct the calibration curve ($\log k'$ vs. $\log K_{ow}$).

Compounds	$\log k'$	$\log K_{ow}$ *lit.*	Reference	Predicted $\log K_{ow}{}^{a}$
p,*p*′-DDT	0.875	5.57	15	5.03
HCB	1.174	5.47	15	5.81
2,4,5-TCB	0.816	4.93	6	4.87
Benzene	−0.247	2.13	16	2.07
Toluene	0.210	2.65	16	3.28
p-Xylene	0.074	3.13	17	2.91
Ethylbenzene	0.140	3.20	17	3.09

[a] K_{ow} values obtained from Eq. (1).

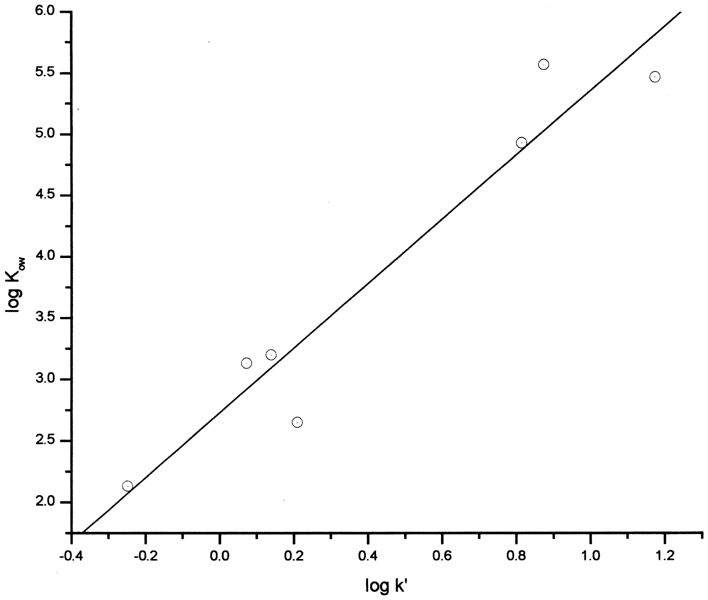

Figure 1. Calibration curve between log k' and $\log K_{ow}$.

RESULTS AND DISCUSSIONS

The data used for the construction of the calibration curve are summarized in Table 1. The linear regression equation resulted from the calibration curve (Fig. 1) is

$$\log \mathrm{K}_{\mathrm{ow}} = 2.724 + 2.633 \log k' \tag{1}$$

The correlation coefficient is 0.963. Toluene and p,p'-DDT deviated slightly from the linear fit.

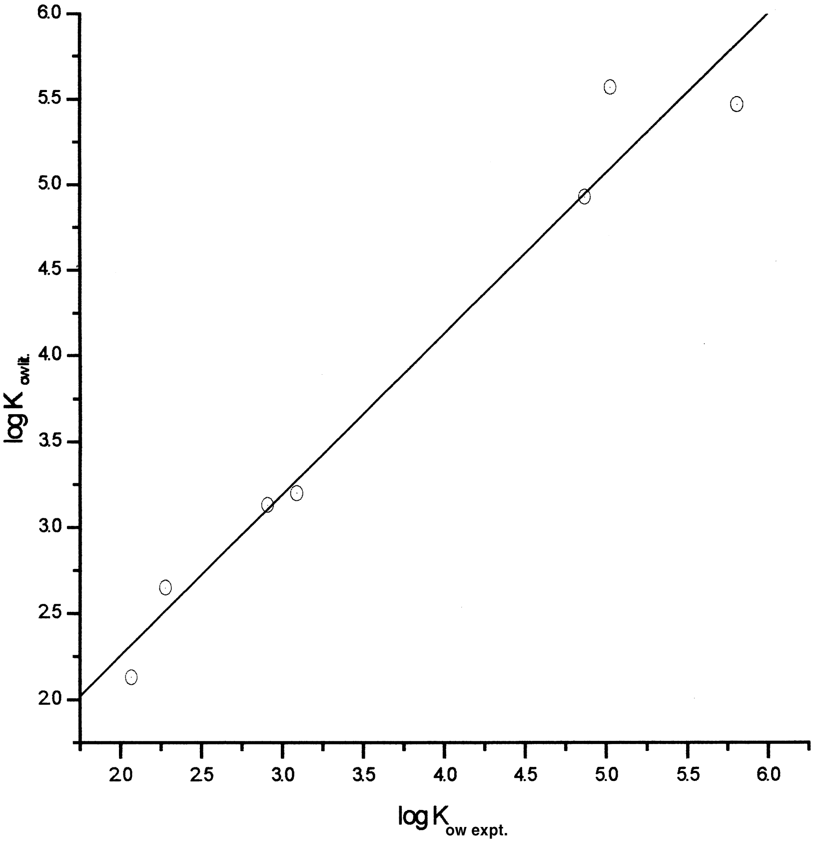

Figure 2. Log K_{ow} used in the calibration curve log K_{ow} from the calibration curve.

The compounds used for the calibration curve are a heterogeneous group including two aromatic halogenated pesticides (HCB and p,p'-DDT), one PCB (2,4,5-TCB), and four aromatic hydrocarbons (benzene, toluene, *p*-xylene, ethylbenzene). The variety of compounds is used to yield a calibration curve that is unbiased towards a single group of compounds.

Figure 2 shows a calibration plot between the HPLC derived $\log K_{ow}$ values ($\log K_{ow}$ *expt.*) using Eq. (1), against the $\log K_{ow}$ values determined by classical methods (K_{ow} *lit.*). This can be useful to eliminate small systematic errors, which may arise due to the column packing. The regression equation obtained from this linear fit is,

$$\log K_{ow\ lit.} = 0.375 + 0.938 \log K_{ow\ expt.} \tag{2}$$

The correlation coefficient is 0.983.

Now, from Eqs. (1) and (2) we get the final regression equation as,

$$\log K_{ow} = 2.931 + 2.471 \log k' \tag{3}$$

With the k' data derived from the experiments, $\log K_{ow}$ values were predicted for 16 PAHs by using the linear regression Eq. (3). The results are summarized

Table 2. Capacity factor and octanol–water partition coefficients for PAHs.

Compounds	$\log k'$	$\log K_{ow}$ *expt.*	$\log K_{ow\ lit.}$[a]
Napthalene	0.158	3.32	3.30
Acenapthylene	0.276	3.61	3.70
Acenapthene	0.338	3.77	3.92
Fluorene	0.417	3.96	4.18
Phenanthrene	0.461	4.07	4.46
Anthracene	0.515	4.20	4.45
Fluoranthene	0.634	4.50	5.20
Pyrene	0.699	4.66	4.88
Chrysene	0.883	5.11	5.86
Benzo(a)anthracene	0.879	5.10	5.91
Benzo(b)fluoranthene	1.079	5.60	5.75
Benzo(k)fluoranthene	1.110	5.43	5.78
Benzo(a)pyrene	1.163	5.81	5.97
Dibenzo(a,h)anthracene	1.220	5.95	6.50
Benzo(ghi)perylene	1.28	6.09	6.90
Indeno(1,2,3-cd)pyrene	1.363	6.30	6.95

[a] $\log K_{ow}$ *lit.* values are obtained from Ref. 18.

in Table 2. Comparisons of $\log K_{ow}$ values for PAHs predicted in this study, with those reported in the literatures, were depicted in Fig. 3. Our values were found to agree well with the previously predicted values in the literatures. The correlation coefficient for this linear fit was 0.975.

In the present study, we were also tried to find out any difference in elution behavior of PAHs in a mixture than there would be if injected individually on RP-HPLC. For this purpose, sixteen standard PAHs were chromatographed by injecting separately, for comparison of the elution of the same PAHs in a standard mixture. The results were summarized in Table 3.

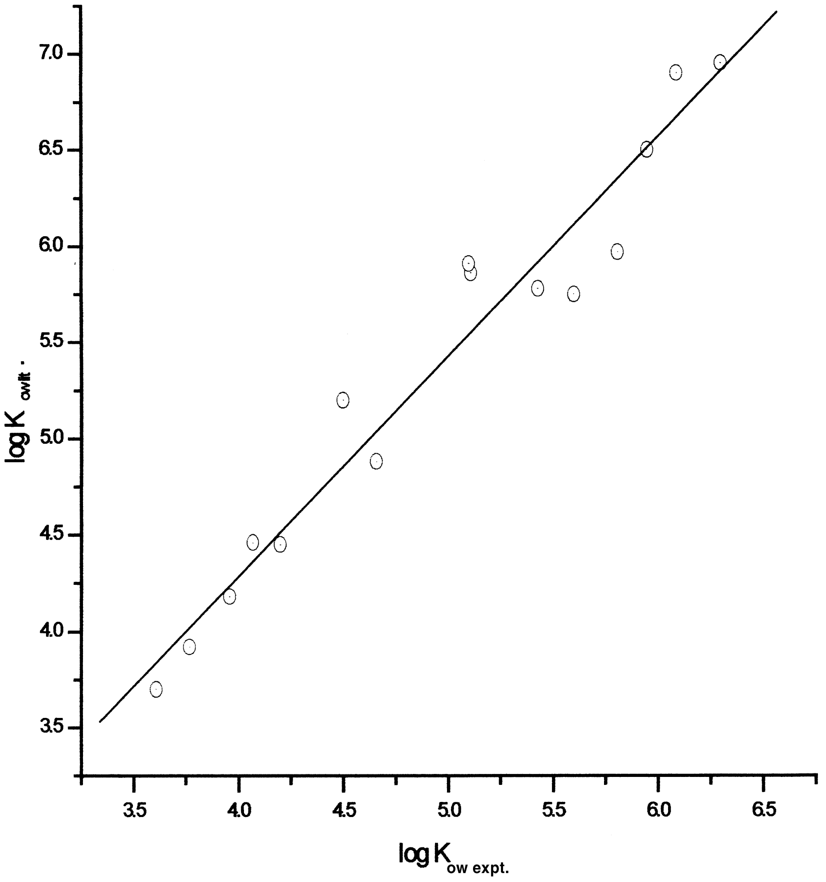

Figure 3. Comparison of K_{ow} estimated from the present study to that obtained from the literature.

Table 3. Comparison of elution behavior of PAHs injected individually and in mixture.

Compounds	$\log K_{ow}$ (individual)	$\log K_{ow}$ (mixture)	[a]Accuracy ratio
Napthalene	3.32	3.29	1.009
Acenapthylene	3.61	3.59	1.006
Acenapthene	3.77	3.79	0.995
Fluorene	3.96	3.93	1.008
Phenanthrene	4.07	4.11	0.990
Anthracene	4.20	4.18	1.005
Fluoranthene	4.50	4.53	0.993
Pyrene	4.66	4.63	1.006
Chrysene	5.11	5.15	0.992
Benzo(a)pyrene	5.10	5.16	0.988
Benzo(b)Fluoranthene	5.60	5.64	0.993
Benzo(k)fluranthene	5.43	5.47	0.993
Benzo(a)pyrene	5.81	5.79	1.003
Dibenzo(a,h)anthracene	5.95	5.91	1.007
Benzo(ghi)perylene	6.09	6.04	1.008
Indeno(1,2,3-cd)pyrene	6.30	6.33	0.995

[a] Accuracy ratio $= \log K_{ow}$ (individual)/$\log K_{ow}$ (mixture).

The predicted $\log K_{ow}$ values were well within the range permitted by statistical variation in the calibration curve. Therefore, $\log K_{ow}$ values for PAHs can be predicted equally well from the standard mixture, which make the method more rapid.

Figure 4 shows a plot of $\log K_{ow}$ values as a function of the number of rings in the PAH compounds. Log K_{ow} increases with the size of the molecules for PAHs. Very little variation in the partition coefficient for PAHs having same number of rings was found. The $\log K_{ow}$ for the three ring PAHs (anthracene and phenanthrene are within a range 4.02–4.07 and that for the four ring PAHs (pyrene, chrysene, and benzo(a)pyrene) are in a range 4.66–5.11. The regression equation obtained from the graph is,

$$\log K_{ow} = 2.071 + 0.689(\text{no. of rings}) \tag{4}$$

The correlation coefficient is 0.974. The relationship predicts that $\log K_{ow}$ increases by 0.689 with an addition of an extra ring to a PAH. The

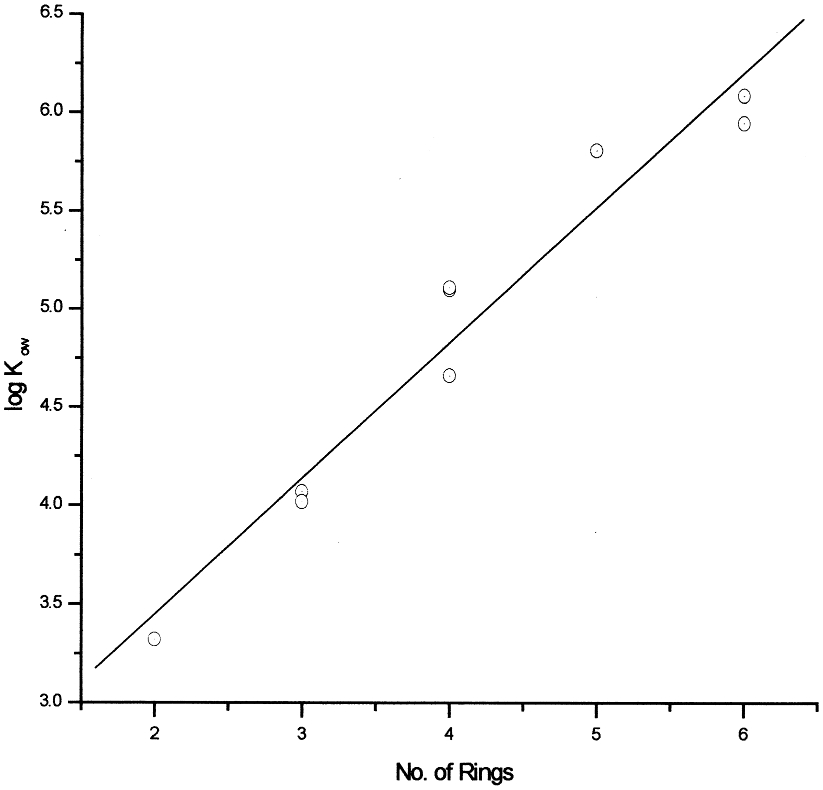

Figure 4. Number of rings in PAH vs. log K_{ow}.

Eq. (4) can be used to predict the log K_{ow} for PAHs when high accuracy is not required.

Figure 5 represents an approach corresponding to that suggested by Seth et al.,[14] plotting log K_{ow} along the x-axis as a reference indicator against the expression log (k'/K_{ow}) along y-axis. This is a way to show if factors other than the hydrophobicity contribute to the partitioning. The regression line for the PAHs is incorporated in the graph. The negative slope (−0.589) is mainly due to the fact that hydrophobicity decreases with an increase in log K_{ow} value. In general the graph shows a good correlation between the log (k'/K_{ow}) and log K_{ow} values ($R = 0.999$). This indicates that the partitioning of PAHs is mainly contributed by its hydrophobicity, rather than any chemical interaction.

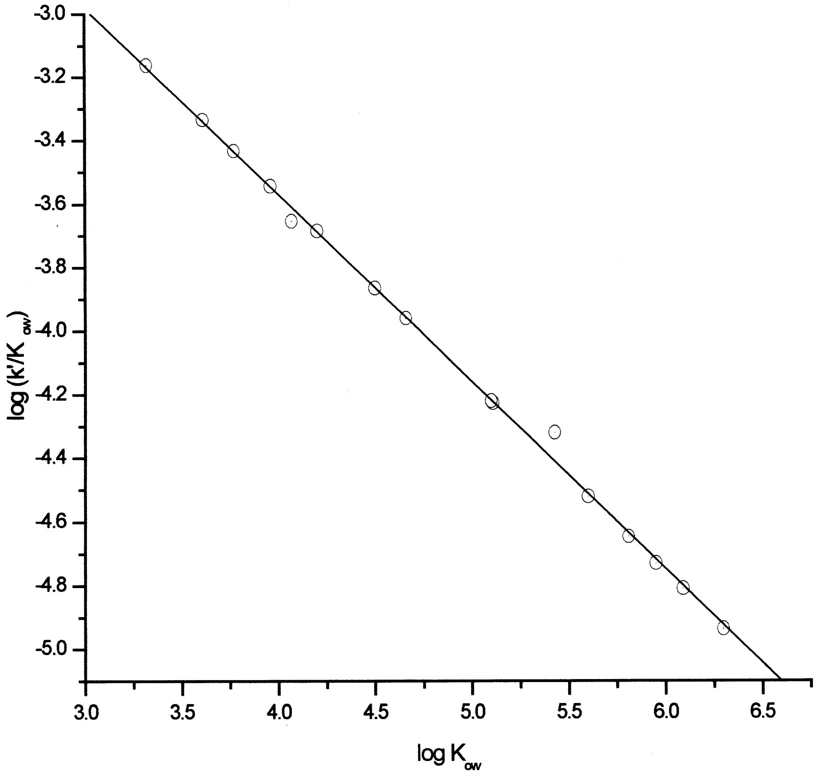

Figure 5. Log K_{ow} vs. log (k'/K_{ow}).

CONCLUSION

The octanol–water partition coefficients for selected PAHs are reported. The RP-HPLC is capable of providing sufficiently accurate and reliable $\log K_{ow}$ values. The elution behavior of PAHs on C18 RP-HPLC is reproducible in standard mixtures and virtually identical with the behavior of individually chromatographed PAHs. Thus, the method is applicable to complex mixtures so that many K_{ow} values can be determined in one experimental run. These results may be useful for assessing the partitioning behavior of individual PAHs in an environmental system.

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