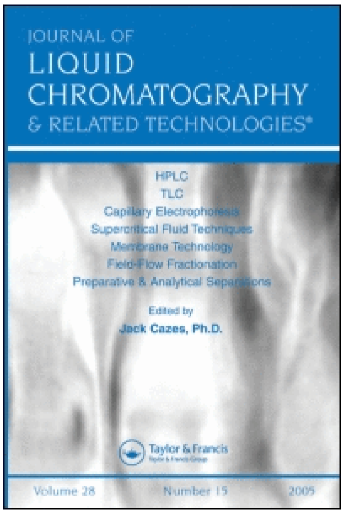

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PARTITION PROPERTIES OF 18 POLYCHLORINATED ORGANIC COMPOUNDS (PCOCs): CORRELATION WITH MOLECULAR STRUCTURAL DESCRIPTORS

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ABSTRACT

The capacity factors (k′) were determined by reversed phase high-performance liquid chromatography (RP-HPLC) on C_{18} column for 18 polychlorinated organic compounds (PCOCs). Quantum chemical parameters and linear solvation energy descriptors were calculated for the tested chemicals and used to develop quantitative structure property relationships (QSPR).

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Results demonstrated that the quantum chemical parameters could be used to predict k' and *n*-octanol/water partition coefficients (Kow) for the test compounds, and the RP-HPLC was a simple and reliable method for prediction of Kow.

INTRODUCTION

The study of the relationship between partition properties and parameters describing molecular structure of solute is one of the most intensively investigated questions in modern chromatography, because it can (i) predict partition behavior, (ii) measure physicochemical parameters, and (iii) lead to an understanding of the partition mechanism. There were many reports on the quantitative relationships for predicting the partition properties based on the molecular structure descriptors (empirical, semi-empirical, and non-empirical), such as linear solvation energy descriptors (1–3), molecular connectivity indices (1,2,4), and quantum chemical parameters (2,5) in RP-HPLC.

Quantum chemical parameter is a kind of non-empirical structural descriptor that can be obtained by the chemical structure and quantum chemical software. Quantum structural descriptors are widely used in the QSPR studies (6–8). According to their significant advantages: they are not restricted to closely related compounds, they can be easily obtained, and describe clearly defined molecular properties.

The linear solvation energy relationship concept, developed by Kamlet *et al.*, (9) is a general approach to describe solvation and partition or related properties in diverse media. Within this approach there are three contributions to the total solute-solvent interaction:

$$\text{Total} = \text{cavity term} + \text{dipolarity/polarizability term} + \text{hydrogen bonding term}$$

The *cavity term* measures the free energy or enthalpy input necessary to separate the solvent molecules, i.e., to overcome solvent-solvent cohesive interactions to provide a suitably sized cavity for the solute. The *dipolarity/polarizability term* measures the effects of solute-solvent dipole-dipole and dipole-induced dipole interactions, and usually is exoergic. The *hydrogen bonding term* measures the exoergic effects of complexation between hydrogen bond donor solvents and hydrogen bond acceptor solutes.

It is well known, that there is a considerable amount of polychlorinated organic compounds (PCOCs), such as organo-chlorine pesticides and polychlorinated biphenyls (PCBs) in our environment. Most of PCOCs are persistent pollutants and highly hydrophobic, resulting in accumulation/concentration in organisms, or in organic phase of soils or sediments. In addition, all of these selected compounds were identified in some of the drinking water resources of China, through the international cooperation project (ICD-DCPL962005) ‘Investigation and risk Assessment of Polychlorinated Organic Compounds in Drinking Water Resources of Developing Regions in Eastern China,’ which was conducted by the European Commission and China. Therefore, further research on these interesting PCOCs is of crucial importance (10).

The major purpose of this paper is to develop statistics significant QSPR equations, based on semi-empirical quantum chemical parameters and linear solvation energy descriptors for the studied chemicals, which can be used to predict the partition properties for structure-related compounds, and to elucidate the partition mechanism for these compounds. Furthermore, it was found that RP-HPLC was a simple, precise, and effective method for predicting octanol/water partition coefficient.

EXPERIMENTAL

Instruments

The HPLC system (Shimadzu, Japan) consisted of a SCL-8A system monitor, a LC-8A pump, a C-R4A integrator, and a SPD-6AV ultraviolet spectrophotometer as the detector.

Reagents

Methanol (G.R., Merck, Germany); doubly distilled water; sodium nitrate (A. R.).

Samples

All of the 18 PCOCs was analytical reagent grade, and there was no interference peak by HPLC. Names of studied chemicals are listed in Table 1.

Determination of Capacity Factors

A Nucleusil7 C_{18} column, 15 cm × 4.6 mm i.d. (made by Shanghai Institute of Organic Chemistry, Academia Sinica) was used. Chromatography was conducted using eluents with the following proportions (V/V) of methanol to water 100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30 (V/V).

Table 1. Names of 18 PCOCs and Part of Calculated Molecular Structural Descriptors*

No.	Name	MW	MR	HLC	q^{+}_{max}	$V_{i/100}$	β_m
1	Hexachlorobenzene	284.78	54.89	1.44	0.1336	1.031	0.04
2	Heptachlor	373.32	76.93	2.14	0.1892	1.845	0.50
3	Octachlorostyrene	379.71	74.75	2.03	0.1370	1.829	0.62
4	Dieldrin	380.91	78.01	4.66	0.1829	1.558	0.86
5	Heptachlor epoxide	389.31	75.08	5.00	0.1897	1.528	0.91
6	Aldrin	364.91	79.76	1.80	4.1338	1.674	0.45
7	2,4′-DDD	320.04	79.97	2.75	0.1190	1.502	0.10
8	4,4′-DDT	354.48	85.32	3.20	0.1203	1.632	0.24
9	2,4′-DDE	318.02	80.27	2.85	0.1196	1.516	0.20
10	4,4′-DDE	318.02	80.27	2.85	0.1192	1.516	0.39
11	2,2′,3,4,4′,5,5′-PCB	360.88	80.02	2.55	0.1330	1.550	0.04
12	2,4,4′-PCB	257.54	65.61	2.16	0.1386	1.190	0.21
13	2,2,′,5,5′-PCB	291.99	70.41	2.29	0.1265	1.280	0.14
14	2,2′,4,5,5′-PCB	326.43	75.22	2.42	0.1326	1.370	0.11
15	2,2′,3,4,4′,5-PCB	360.88	80.02	2.55	0.1329	1.460	0.12
16	2,2′,4,4′,5,5′-PCB	395.32	84.83	2.68	0.1629	1.460	0.06
17	Pentachlorotoluene	264.36	55.12	1.27	0.1288	1.040	0.01
18	2,4′-DDT	354.48	85.32	3.20	0.1208	1.620	0.24

*MR: molar refractivity, MW: molecular weight, HLC: Henry constant, q^{+}_{max} maximum positive atomic charge, $V_{i/100}$: van der Waals molecular volume, β_m: the ability of solute accepts proton in hydrogen bond interaction.

The flow rate was 0.8 mL/min. An aqueous solution of sodium nitrate was used for measurement of dead time. All measurements were made at least in duplicate. The average reproducibility of each determination was better than 1.0% relative.

Calculation of Molecular Structural Descriptors

Molecular geometry was optimized and parameters were calculated using the semi-empirical orbital MOPAC97 procedures according to methods AM1 (11).

Linear solvation energy relationship (LSER) parameters $V_{i/100}$, π^*, β_m and α_m, known as 'solvatochromic parameter', could be used to estimate the different interaction terms, and were calculated according to a handy estimation method 'Rule of Thumb' (12).

Some of calculated parameters entering equations are listed in Table 1. The lgKow data taken from literatures (13–15) are included in Table 2. In general, the

Table 2. The Observed Predicted Values and Residuals of Eqs. 2-6

	$\log k'_W$					$\log K_{ow}$						
		eq. 2		eq. 4			eq. 3		eq. 5		eq. 6	
No.	Obs.	Pred.	Res.	Pred.	Res.	Obs.	Pred.	Res.	Pre.	Res.	Pre.	Res.
1	6.155	6.230	−0.074	6.186	−0.030	6.18	6.11	0.07	6.16	0.02	6.16	0.02
2	7.279	7.474	−0.195	7.201	0.077	6.69	6.66	0.03	6.64	0.05	6.66	0.03
3	7.333	7.481	−0.148	6.876	0.457	6.55	6.63	−0.08	6.47	0.08	6.69	−0.14
4	5.590	5.598	−0.008	5.609	−0.019	5.82	5.84	−0.02	5.85	−0.03	5.91	−0.09
5	5.226	5.200	0.027	5.413	−0.186	5.65	5.62	0.03	5.75	−0.10	5.74	−0.09
6	6.709	6.709	0.000	6.878	−0.169	6.50	6.50	0.00	6.48	0.02	6.41	0.09
7	6.746	6.900	−0.154	7.261	−0.514	6.57	6.57	0.00	6.68	−0.11	6.42	0.15
8	6.822	7.057	−0.235	7.266	−0.443	6.47	6.61	−0.14	6.68	−0.21	6.46	0.01
9	6.839	6.828	0.012	7.061	−0.221	6.59	6.55	0.04	6.58	0.01	6.47	0.12
10	6.915	6.828	0.087	6.611	0.303	6.54	6.55	−0.01	6.35	0.19	6.50	0.04
11	7.399	7.284	0.115	7.527	−0.128	6.65	6.64	0.01	6.82	−0.17	6.72	−0.07
12	6.220	6.151	0.069	6.194	0.026	6.14	6.25	−0.11	6.16	−0.02	6.19	−0.05
13	6.444	6.532	−0.088	6.592	−0.148	6.37	6.38	−0.01	6.35	0.02	6.29	0.08
14	7.018	6.907	0.111	6.896	0.122	6.50	6.51	−0.01	6.50	0.00	6.55	−0.05
15	7.583	7.284	0.299	7.105	0.478	6.65	6.64	0.01	6.61	0.04	6.80	−0.15
16	7.844	7.652	0.192	7.247	0.597	6.86	6.77	0.09	6.68	0.18	6.91	−0.05
17	6.335	6.265	0.070	6.280	0.056	6.20	6.18	0.02	6.21	0.01	6.24	−0.04
18	6.978	7.057	−0.079	7.235	−0.257	6.70	6.61	0.09	6.66	0.04	6.53	0.17

more recent compilation contained the more reliable data presently available and, in most instances, the median or frequently encountered value was used when several measured values were available for a given chemical. The regression analyses were performed using the 'Statgraphics' program (version 4.0, Statistical Graphic Cooperation, Englewood Cliffs, NJ, USA, 1987).

RESULTS AND DISCUSSION

The relationship between $\log k'$ and methanol concentration in mobile phase given by Snyder *et al.* (16) is as follows:

$$\log k' = \log k'_W + S\varphi_{CH3OH} \qquad (1)$$

Where $\log k'_W$ is the intercept of the above equation and represents the k' value for a compound if pure water is used as eluent, S is slope of the regression curve, and φ denotes the volume percentage of methanol in the eluent. The $\log k'$ for each studied compound was plotted against the volume fraction of methanol in the eluent. Excellent linear relationships were obtained.

In order to describe the relationship between the retention indices of tested chemicals and the calculated structural parameters, stepwise regression analyses were performed, and the obtained QSPR equations are presented below:

AM1:

$$\begin{aligned}\mathrm{logk'_W} &= 2.531(0.365) + 0.060(0.006)\mathrm{MR} - 0.788(0.053)\mathrm{HLC} \\ &\quad - 0.293(0.045)\mathrm{q^{+}_{max}} + 0.006(0.001)\mathrm{MW} \\ n = 18, R &= 0.978, R^2_{adj} = 0.944, s = 0.159, F = 72.58, p = 0.0000\end{aligned} \quad (2)$$

$$\begin{aligned}\mathrm{logKow} &= 4.635(0.143) + 0.036(0.002)\mathrm{MR} - 0.342(0.021)\mathrm{HLC} \\ &\quad - 0.097(0.019)\mathrm{q^{+}_{max}} \\ n = 18, R &= 0.981, R^2_{adj} = 0.953, s = 0.068, F = 117.18, p = 0.0000\end{aligned} \quad (3)$$

LSERs:

$$\begin{aligned}\mathrm{logk'_W} &= 3.615(0.566) - 2.364(0.340)\beta_\mathrm{m} + 2.584(0.411)\mathrm{V_{i/100}} \\ n = 18, R &= 0.890, R^2_{adj} = 0.765, s = 0.325, F = 28.67, p = 0.0000\end{aligned} \quad (4)$$

$$\begin{aligned}\mathrm{logKow} &= 4.905(0.188) - 1.195(0.113)\beta_\mathrm{m} + 1.263(0.137)\mathrm{V_{i/100}} \\ n = 18, R &= 0.947, R^2_{adj} = 0.882, s = 0.108, F = 64.81, p = 0.0000\end{aligned} \quad (5)$$

Where n is the number of chemicals, R is the correlation coefficient adjusted by degree of freedom, s is the standard error of estimates, F is the F-test value, p is the significance level; the number in parentheses is the standard error associated with each coefficient.

Among the eqs. 2-5, eqs. 2 and 3 are the most significant. Both of them have high R^2_{adj} and low SE values, which indicated that $\mathrm{logk'_W}$ or logKow could be predicted by models based on quantum chemical descriptors. However, linear solvation energy parameters are less effective than quantum chemical descriptors in predicting retention indices and partition coefficient for studied compounds. The predicted $\mathrm{logk'_W}$ and logKow values and their corresponding residuals for the test chemicals, are shown in Table 2. Plots of predicted $\mathrm{logk'_W}$ and logKow versus their corresponding observed values are shown in Figure 1, and the frequency distribution of residuals are shown in Figure 2. It was found that the residuals of

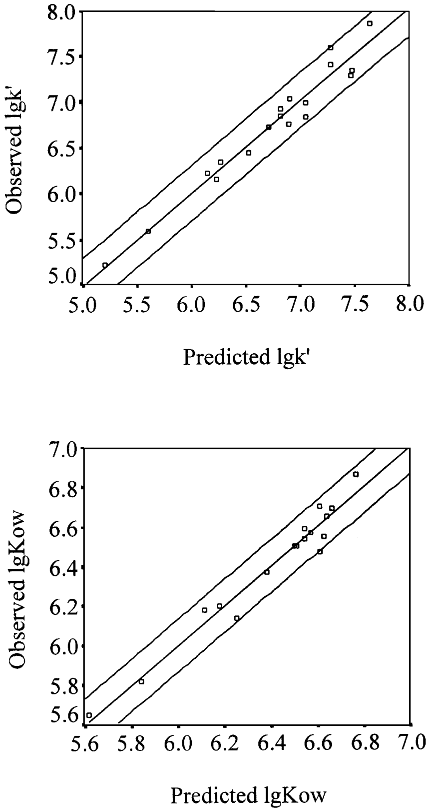

Figure 1. Plots of observed and predicted $\log k'_W$/logKow values according to eqs. 1 and 2.

logKow and $\log k'_W$ conform to normal functions $(-1.1\times 10^{-15}, 0.0167^2)$ and $(-2.7\times 10^{-15}, 0.0328^2)$, respectively. Since there were only 18 samples, the K-S method was selected to test the goodness-of-fit, and the results are listed in Table 3, which indicated that there was no distinct discrepancy between the frequency distribution of residuals and normal function. In addition, there was no serious collinearity among the variables entering the obtained equations according to the correlation matrices.

Furthermore, the Student *t* values for partial correlation coefficient are 9.653, −15.000, −6.559, and 4.045 for MR, HLC, q^+_{max} and MW descriptors in eq. 2, respectively. While the *t*-values are 16.528, -16.304, and −5.211 for MR, HLC and q^+_{max} descriptors in eq. 3, respectively. This indicated that descriptors

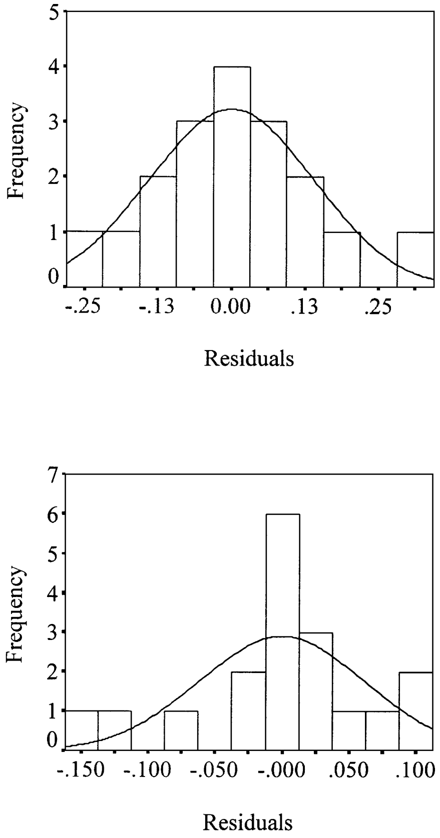

Figure 2. Plots of frequency distribution according to eqs. 1 and 2, respectively.

Table 3. The Results of K-S Test for Eqs. 2 and 3

		eq. 2	eq. 3
Most Extreme Differences	Absolute	0.093	−0.200
	Positive	0.093	0.083
	Negative	−0.087	−0.200
Kolmogorov-Smimov Z		0.394	0.847
Asymp. Significance Level (2-tailed)		0.998	0.470

molar refractivity (MR) and Henry law constant (HLC) were the most significant factors for both $\log k'_W$ and logKow. MR, provides information about the bulkiness or polarizability of the solute, and may be related to the interaction between the solute molecule and the stationary phase occurring in reversed-phase liquid chromatography. The larger the solute molecule, the stronger the solute-adsorbent interaction. Similarly, in the octanol/water system, the solute molecule with large bulkiness or polarizability tends to partition into octanol phase. HLC, determines the ratio the solute evaporates from solution, for a closed system. The higher HLC means lower concentration in solution, that is, there are smaller parts that can partition into methanol or octanol phase. In addition, the q^+_{max} descriptor is related to the ability of the solutes to participate in hydrogen-bonding interactions with eluent molecules. The descriptor MW reflects the bulkiness of solute molecule.

The above results can also be obtained from eqs. 4 and 5, based on linear solvation energy relationships. Descriptors $V_{i/100}$ and β_m represent the molecular eigen-volume and the ability of the solute molecule to accept a proton in forming a hydrogen bond, respectively. The larger the $V_{i/100}$ is, the more parts of solute molecules partition into the organic phase. The higher the β_m is, the easier the solute molecule accepts a proton, and more parts partition into the solvent phase.

It can be concluded that the partition process of solute in an octanol-water system is similar to that of the stationary-mobile phase of a HPLC system. Therefore, the relationship between logKow and $\log k'_W$ was developed as eq. 6.

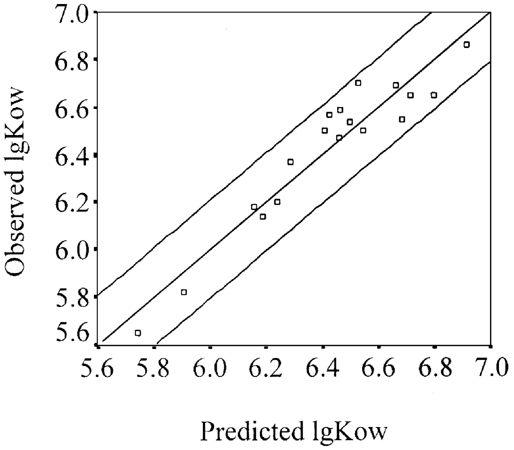

Figure 3. Plot of observed and predicted logKow values from eq. 6.

This indicated that the logKow values of these PCOCs could be predicted, with their $\log k'_W$ values obtained easily and precisely (shown in Figure 3).

$$\log Kow = 3.406(0.241) + 0.447(0.036)\log k'_W$$
$$n = 18, R = 0.953, R^2_{adj} = 0.902, SE = 0.098, F = 158.24, p = 0.0000 \tag{6}$$

In summary, the obtained correlations between quantum chemical descriptors and the retention indices or octanol/water partition coefficient for 18 PCOCs were very good and could be used to predict physicochemical properties of the structure-related molecules. Compared with the linear solvation energy relationship, the quantum chemical method was more effective in predicting properties for studied compounds. Besides, the quantum parameters have clear physicochemical interpretations. Retention in RP-HPLC is found to be the net effect of bulkiness-dependent on polarizability interactions and electrostatic or hydrogen bonding interaction involving solute molecules and molecules of both mobile and stationary phases. This conclusion agreed with the previous result (17).

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