THE CALCULATION OF POLLUTANTS OCTANOL/WATER PARTITION COEFFICIENT. (I) CHLORODERIVATIVES

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abstract: To develop correlations between **T**hreshold **L**imit **V**alues (TLV's) of different pollutants and their physical-chemical properties the calculation of partition coefficient is a very important step. In this work were calculated the values of log $K_{o/w}$ for a group of 20 chloroderivatives using the method of Ghose, Pritwchett and Crippen. The obtained values are discussed in correlation with the chemical bond specific of these pollutants. Linear regression equations were obtained for the dependence log TLV = f (log $K_{o/w}$).

key words: chloroderivatives pollutants, TLV, octanol-water partition coefficient, QSPR.

Introduction

The coefficient of water/oil distribution, also called the partition coefficient is the ratio of the solubility of a chemical in water to its solubility in oil [1]. It is abbreviated as $K_{o/w}$; it may be also expressed as its logarithm, log $K_{o/w}$. It is used to indicate how easily human or other organism can absorb, or store a material. For this reason it is a very important thermodynamic characteristic of individual pollutants [2] being used as descriptor in some QSAR/QSPR studies.

Some different experimental methods are used to determine the partition coefficient between two nonmiscible phases [2,3].

The partition coefficient may be also obtained by different calculation methods [4,5]. Because octanol is a liquid which posses similar kinetic and transfer properties as human fluids, the most used reference for $K_{o/w}$ or log $K_{o/w}$ is those corresponding to octanol/water system. We are interested in developing of correlations between Threshold Limits Values, TLV's of different pollutants with the physical chemical properties of those pollutants [7,10]. This situation urges systematically use of the precise standardised procedure of calculation for $K_{o/w}$ evaluation. The aim of this work is to explain our procedure of calculation for the class of 20 pollutants, which are organic chloroderivatives compounds, and to discuss obtained values.

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Calculation details

The 20 studied pollutants are grouped in the Table 1 as follows: positions 1-10 correspond to saturated compounds (with only δ type bonding), positions 11-20 to chloroaromatic (with δ and conjugated π bonds). The compounds are disposed in the order of increasing molecular weight and chlorine atoms number.

We used for calculation of log $K_{o/w}$ the incremental method of Ghose, Pritwchett and Crippen implemented in Hyperchem [11,12]. For the selected chloroderivative compounds we considered the molecular structures optimized by mechanics molecular method with the MM+ force field. The electrostatic term was calculated by bond dipole approximation. Geometry optimisation was done with the Polack-Ribiere algorithm and a 0.001 Kcal/mol·Å gradient.

Results and discussion

All studied pollutants can be considered volatile organic compounds (VOC) because are satisfied the following restrictions for the molecular weight M, density, d (g/cm^3), melting point T_m (°C), boiling point T_b (°C):

$30 < M < 300$; $0.6 < d < 2$; $-190°C < T_m < 180°C$; $-100°C < T_b < 300°C$.

Obtained results for this class of pollutants are listed in Table 1.

Table 1. Calculated values of log $K_{o/w}$

No. crt.	Compound	TLV (mg/m^3)	M (g/mol)	log $K_{o/w}$
1	*Di*chloromethane	174	85	1.15
2	1,1 *di*choroethane	405	99	1.16
3	1,2 *di*chloroethane	30	99	1.59
4	1,2 *di*chloropropane	100	113	2.00
5	Chloroform	10	119.5	1.61
6	1,1,1 *tri*chloroethane	555	133.5	2.04
7	1,2,3 *tri*chloropropane	100	147.5	2.36
8	*C*arbon tetrachloride	30	154	3.37
9	1,1,2,2 *tetra*chloroethane	20	168	2.06
10	*Hexa*chlorocyclohexane	0.3	291	4.65
11	1,4 *di*chlorobenzene	122	147	3.08
12	Chlorobenzene	47	112.5	2.56
13	*Para* chlorotoluene	150	126.5	3.03
14	1,2 *di*chlorobenzene	122	147	3.08
15	1,2,4 *tri*chlorobenzene	15.1	181.5	3.60
16	*Hexa*chlorobenzene	0.5	285	5.15
17	2 *mono*chlorostyrene	50	138.5	3.21
18	*B*enziltrichloride	2	195.5	3.49
19	2,6 *di*chlorostyrene	30	173	3.73
20	Benzilchloride	5	126.5	2.66

Analysing the obtained values we can observe two peculiarities:

1. The value of log $K_{o/w}$ increase with increasing of M (and also with the increased number of chlorine atoms) in the series of saturated compounds (no. 1-10) *i.e.* its

hydrophobicity increase. As consequence these pollutants will be absorbed in lipoid tissues. The obtained for log TLV = f (log $K_{o/w}$) dependence is:

$$\log TLV = 3.0706 - 0.6540 \log K_{o/w};\ r^2 = 0.5533$$

2. In the second part of table 1 (no. 11-20) where are grouped the chloroderivatives of arenes, in general, the values of log $K_{o/w}$ are increased. The dependence on molecular weight is not so pronounced and the hydrophobicity varies in larger limits. These pollutants will be absorbed in more significant measure in lipoid human's tissues. This explains great incidence of cancer in presence of these pollutants, their greater toxic risk. As consequence, TLV's for this category of chlorocompounds are more reduced according to data extracted from [9] and statements [13]. In this case the obtained logTLV = f (log $K_{o/w}$) dependence is:

$$\log TLV = 3.6374 - 0.7128 \log K_{o/w};\ r^2 = 0.4311$$

Conclusions

1. In this work are calculated log $K_{o/w}$ values for 20 selected VOC chloroderivatives pollutants by incremental method of Ghose, Pritwchett and Crippen.
2. For the compounds 1-10 (see table 1) which are saturated chloroderivatives the obtained log $K_{o/w}$ values are smaller than those for the aromatic chloroderivatives 11-20. As consequence TLV's for the last class of pollutants is more reduced. In consequence they are more toxic.
3. The calculated regression coefficients of the logTLV = f (log $K_{o/w}$) dependence are better for the aliphatic chloroderivatives.

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