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COMPARATIVE SURVEY OF CALCULATED AND EXPERIMENTAL OCTANOL/WATER PARTITION COEFFICIENTS FOR CHLORINATED POLLUTANTS

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abstract A comparative analysis of water/octanol partition coefficients calculated by the incremental method of Ghose, Pritwchett and Crippen (**GPC**) and experimentally determined values stored in the EPI Suite v3.20 was made for 37 chlorinated pollutants. The octanol/water partition coefficient may serve as descriptor for threshold limits values (TLV's) of these pollutants which present a special interest in occupational risk evaluation.

key words chlorinated pollutants, octanol/water partition coefficient, computational method GPC, EPI v3.20.

Introduction

The partition coefficient between octanol-water is defined as the ratio of solubility of a chemical in water to its solubility in octanol [1]. Abbreviated as $K_{o/w}$ (or as log $K_{o/w}$) is the most used property to show how easily human or other organisms can absorb or store a chemical [2-4].

We are interested in searching correlations between threshold limit values (TLV's) of pollutants with different physical chemical properties of these pollutants [5-10] in particularly with log $K_{o/w}$.

This action may be motivated by the possibility of TLV's prediction on this basis in case of some pollutants [2]. Because the TLV's present a special interest in occupational risk evaluation, this perspective urges a systematic use of a precise standardized procedure for calculation of log $K_{o/w}$. In this work we extended the group of the studied chloroderivatives in comparison with the precedent work [1] to 37 compounds to assure the conditions of a statistical representative. Now we try also a comparative survey of calculated log $K_{o/w}$ values using incremental methods [4,5] and those experimental obtained from EPI Suite v 3.20.

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Details on calculation method and data selection

The 37 studied pollutants are grouped as follows: in the Table 1, the positions 1-17 correspond to saturated chloro-compounds (with only σ type bonding), in the Table 2 the positions 1-9 correspond to chloro alkenes (with σ and π isolated type bonds) and in the Table 3 are given 11 aryl chloro compounds (with σ and π conjugated type bonds).

Table 1 Comparison of EPI Suite v3.20 and GPC log $K_{o/w}$ data for saturated chlorocompounds

No.	Compound	M (g/mol)	log $K_{o/w}$		TLV-TWA (CMA) (mg/m^3)
			GPC	EPI	
1	methyl chloride	50.49	0.88	0.91	75
2	ethyl chloride	64.51	1.22	1.43	1000
3	isopropyl chloride	78.54	1.64	1.9	400
4	*di*chloro methane	84.93	1.15	1.25	174
5	1,1 *di*chloro ethane	98.96	1.16	1.79	405
6	1,2 *di*chloro ethane	98.96	1.59	1.48	30
7	1,2 *di*chloro propane	112.99	2.00	1.98	100
8	*chloroform*	119.38	1.61	1.97	10
9	1,1,1 *tri*chloro ethane	133.40	2.04	2.49	1000
10	1,2,3 *tri*chloro propane	147.43	2.36	2.27	100
11	carbon *tetra*chloride	153.82	3.37	2.83	30
12	1,1,1,2 *tetra*chloro ethane	167.85	2.42	-	20
13	1,1,2,2 *tetra*chloro ethane	167.85	2.06	2.39	20
14	*penta*chloro ethane	202.29	2.65	3.22	40
15	*hexa*chloro ethane	236.74	3.25	4.14	5
16	*hexa*chloro cyclohexane	290.83	4.65	-	0.30
17	chloro bromo methane	129.38	1.03	-	700

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 chlorinated compounds we considered the molecular structures optimized by molecular mechanics method with the MM+ force field. The electrostatic term was calculated by bond dipole approximation. Geometry optimization was done with the Polack-Ribiere algorithm and a 0.001 Kcal/mol·Å gradient.

The TLV's listed values correspond to the Romanian General Norms for Work Protection from 2002, actualized in rapport with European Union Norms [13] with the exception of compound 6 from Table 2 whose values were obtained from [14].

Table 2 Comparison of EPI Suite v3.20 and GPC $K_{o/w}$ data for alkenes derivatives

No.	Compound	M (g/mol)	Log $K_{o/w}$		TLV-TWA (CMA) (mg/m^3)
			GPC	EPI	
1	vinyl chloride	62.5	1.01	-	7.77
2	allyl chloride	76.52	1.62	-	3
3	metallyl chloride	90.55	1.78	-	80
4	1,1 *di*chloro ethene	96.94	1.82	2.13	20
5	1,2 *di*chloro etene	96.94	0.89	2.00	200
6	1,3 *di*chloro propene	110.97	1.36	2.04	4.5
7	*tri*chloro etylene	131.39	1.71	2.42	100
8	*per*chloro etylene	165.83	2.52	3.40	50
9	chloroprene	88.54	1.44	-	30

In the 4th column of each table are given the calculated log $K_{o/w}$ values in parallel with those extracted with EPI Suite v.3.20. The majority of the experimentally determined log$K_{o/w}$ were obtained by the UV-VIS absorption method [5].

Table 3 Comparison of EPI Suite v3.20 and GPC log $K_{o/w}$ data for aryl chlorocompounds

No.	Compound	M (g/mol)	log $K_{o/w}$		TLV-TWA (CMA) (mg/m^3)
			GPC	EPI	
1	chloro benzene	112.56	2.56	2.84	47
2	benzyl chloride	126.58	2.66	2.30	5
3	*orto* chloro toluene	126.58	3.03	-	150
4	*para* chloro toluene	126.58	3.03	3.33	150
5	2 chloro styrene	138.6	3.21	-	50
6	1,2 *di*chloro benzene	147	3.08	3.43	122
7	1,4 *di*chloro benzene	147	3.08	3.44	122
8	2,6 *di*chloro styrene	173.04	3.73	-	30
9	benzyl *tri*chloride	195.48	3.49	-	2
10	1,2,4 *tri*chloro benzene	181.45	3.60	4.02	15.1
11	*hexa*chloro benzene	284.78	5.15	5.73	0.5

Results and Discussion

The majority of studied pollutants (s. tables 1-3) may be considered volatile organic compounds (VOC) because are satisfied the following restrictions for the molecular weight M (g/mol), density d (g/cm^3), melting point T_m (°C) and boiling point T_b (°C):

$$30 < M < 300$$

$$0.6 < d < 2$$

$$-190 < T_m < 180$$

$$-100 < T_b < 300$$

Compounds like hexachlorethane and hexachlorobenzene posses some properties (see tables 1–3) which surpass above mentioned restrictions. From the comparative analysis of the presented data results followings:

1. The value of the $K_{o/w}$ increases with the molecular weight M (and with the number of chlorine atoms) in the series of saturated compounds (Table 1). This means that the hydrophobicity increases in the same direction. As consequence these pollutants will be absorbed in the lipoid tissues. We can observe that EPI Suite v 3.20 values for log $K_{o/w}$ are higher then that calculated by GPC method with maximum 0.6 log units. Exceptions are 1,2 dichloroetahane, 1,2 dichloropropane, 1,2,3-trichloropropane and carbon tetrachloride where situation is inverse, but differences are reduced. In the case of 1,1,1,2 tetrachloro ethane and of hexachloro cyclohexane there are no log $K_{o/w}$ experimental data and this shows the need of GPC calculations.

2. In the case of chlorocompounds derived from alkenes (s. Table 2) we observed that for the compounds 1-3 and 9 the log $K_{o/w}$ data were absent from EPI Suite v3.20, but the experimental values for the compounds 4-8 are in general much more higher than those calculated by GPC method. In this case the hydrophobic character is maintained at medium level.

3. In the case of aryl chloro compounds (s. Table 3) EPI Suite v.3.20 data for compounds 3, 5, 8 and 9 were absent. Here, systematically the EPI Suite v.3.20 data are higher than those calculated by GPC method; differences cover the interval of 0.27-0.58 log $K_{o/w}$ units. The hydrophobic character of these compounds is maximal. These pollutants will be absorbed in more significant measure in lipoid human's tissues. This explains great incidence of the cancer induced by presence of these pollutants, their greater toxic risk. As consequence TLV's for this category of chlorocompounds are more reduced, according with data extracted from [9] and statements from [15]

Conclusions

1. In this work for a number of 37 chloro compounds, systematized in 3 classes, we made a comparative analysis of log $K_{o/w}$ values, calculated by incremental GPC method and those comprised in EPI Suite v 3.20 base data.

2. The deviation between EPI and GPC log $K_{o/w}$ values is generally positive.

3. From this survey results that the level of log $K_{o/w}$ values after the two mentioned sources is higher for aryl chloro compounds, which are the most hydrophobic and toxic from the 3 analyzed classes.

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