ESTIMATION OF BIO-ACCUMULATION BY A GROUP CONTRIBUTION METHOD

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ABSTRACT

The majority of organic pollutants, after their dispersion in water then their ingestion, have a strong tendency to accumulate in greases. That is due to the hydrophobic character of these molecules.

To have an idea on the capacity of a substance to accumulate in the alive beings according to their lipidic mass, the modeling of the pollutant behaviour was made by considering its partition coefficient between n-octanol (representing the lipidic mass) and water. Its knowledge represents a very significant information for the petrochemical and the pharmaceutical industries.

To dissipate any doubt about confidence concerning the obtained results, it is considered useful to check the effectiveness of UNIFAC method on the monomethylbenzoïc acid such as, for example, the 3-methylbenzoïc acid whose n-octanol – water partition coefficient is already listed in the literature.

The small deviations observed between the n-octanol–water partition coefficients listed in the literature and the one calculated according UNIFAC method encouraged us to apply it in order to predict the n-octanol–water partition coefficient of the dimethylbenzoïc acid.

Keywords: octanol–water partition coefficient, group contribution model, UNIFAC method, bioaccumlution, dimethylbenzoïc acid

INTRODUCTION

Generally, the bio-accumulation term indicates the phenomenon of accumulation of the chemical substances in the alive beings either directly starting from the medium, or indirectly *via* the food chain: that is due to the hydrophobic character of the molecules.

To have an idea of the capacity of the product to accumulate in an organism, it is considered that the behavior of the lipidic mass is well represented by the n-octanol and, one determines the n-octanol–water partition coefficient because it is the most reliable parameter. It corresponds to the ratio of the solute concentration in the two not mixed liquids at equilibrium, namely n-octanol and water. Thus, the substances with strong value of the partition coefficient (easily soluble in n-octanol and less soluble in water) accumulate in the organisms. With this intention, UNIFAC method (Fredenslund *et al.*, 1975; 1977; Gmehling *et al.*, 1978; 1982; Belhachemi *et al.*, 1996; Belhachemi & Ufnalsky, 1998) was used to estimate the bio-accumulation in form of the n-octanol–water partition coefficient noted K_{ow} (Belhachemi, 2003; Yaws, 1999; Sangster, 1989; Li *et al.*, 1995; Derawi *et al.*, 2001; Marrero & Gani, 2002).

METHOD

For a component ″i″ in the solution enclosing several components, the activity coefficient is composed of two terms:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{1}$$

with :

- $\ln \gamma_i^C$: the combinatorial contribution; due mostly to difference in molecular size and shape; it is given by :

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\Theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{X_i} \sum_j^{const} X_j l_j \tag{2}$$

where :

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \tag{3}$$

Z (the coordination number) is taken to be 10.

To define the different parameters which take part in the formula (3), we consider a mixture which the mole fraction of component ″i″ is X_i. A molecule ″i″ can be marked by a volume r_i and a surface q_i :

$$r_i = \sum_k^{Groupes} \nu_k^{(i)} R_k \;\; ; \;\; q_i = \sum_k^{Groupes} \nu_k^{(i)} Q_k \tag{4}$$

where :

- $\nu_k^{(i)}$ is the number of groups of type k in molecule ″i″ ;
- R_k and Q_k represent the volume and surface parameters of the group k, they are obtained from the VAN DER WAALS group volumes and surface areas V_k and A_k :

$$R_k = \frac{V_k}{V_{CH_4}} \;\; ; \;\; Q_k = \frac{A_k}{A_{CH_4}} \tag{5}$$

V_{CH_4} and A_{CH_4} are the normalization factors.

So, every component intervene in the mixture by :

- Its volume fraction

$$\Phi_i = \frac{r_i X_i}{\sum_j^{Const} r_j X_j} \qquad (6)$$

- Its area fraction

$$\Theta_i = \frac{q_i X_i}{\sum_j^{Const} q_j X_j} \qquad (7)$$

♦ $\ln \gamma_i^R$: the residual contribution, arising mostly from differences in intermolecular forces of attraction.

$$\ln \gamma_i^R = \sum_k^{Groupes} \nu_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \qquad (8)$$

where :

- $\nu_k^{(i)}$, always an integer, is the number of groups of the type k in molecule ″i″ ;
- Γ_k is the residual activity coefficient of group k in the solution ;
- $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type ″i″.

The coefficients Γ_k and $\Gamma_k^{(i)}$ are related to the composition and temperature according to following expression :

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m^{Groupes} \Theta_m \Psi_{mk} \right) - \sum_m^{Groupes} \left(\Theta_m \Psi_{km} / \sum_n^{Groupes} \Theta_n \Psi_{nm} \right) \right] \qquad (9)$$

with :

- Θ_m is the area fraction of group m, it is equal to :

$$\Theta_m = \frac{Q_m X_m}{\sum_n^{Groupes} Q_n X_n} \tag{10}$$

where X_m, which represent the mole fraction of group m in the mixture, is given by :

$$X_m = \frac{\sum_i^{Const} \nu_m^{(i)} X_i}{\sum_i^{Const} \sum_n^{Groupes} \nu_n^{(i)} X_i} \tag{11}$$

where $\nu_m^{(i)}$ and $\nu_n^{(i)}$ are respectively the number of groups of type m and n in molecule ″i″, X_i is the mole fraction of component ″i″.

- Ψ_{nm} represent the interaction parameter between groups n and m, it is given by :

$$\Psi_{nm} = \exp\left[-\frac{U_{nm} - U_{mm}}{RT}\right] = \exp\left(-a_{nm}/T\right) \tag{12}$$

where U_{nm} and U_{mm} designate respectively the energy of interaction between groups m and n on the one hand and, m and m on the other hand. So U_{mm} is different from U_{nn}; it comes that every pair of groups is characterized by two interaction parameters a_{nm} and a_{mn} $\left(a_{nm} \neq a_{mn}\right)$. The last parameters, determined in most cases from liquid-vapor equilibrium, constitute with the volume and surface parameters of groups, UNIFAC data bank.

RESULTS AND DISCUSSION

The n-octanol–water partition coefficient K_{ow} is defined as :

$$K_{ow} = \frac{C_i^o}{C_i^w} \tag{13}$$

where C_i^o and C_i^w are the concentrations of solute (i) in the organic phase (o) and the aqueous phase (w), respectively.

The equation (13) can be written in the following form (Derawi *et al.*, 2001) :

$$K_{ow} = 0.151(\gamma_i^{w,\infty} / \gamma_i^{o,\infty}) \tag{14}$$

where $\gamma_i^{w,\infty}$ and $\gamma_i^{o,\infty}$ are the infinite dilution activity coefficients in the water and n-octanol, respectively.

Equation (14) is applied in order to determine the n-octanol–water partition coefficient of the dimethylbenzoïc acid. With this intention, it is a must, as a preliminary, to test the effectiveness of UNIFAC method on the monomethylbenzoïc acid such as for example the 3-methylbenzoïc acid whose the n-octanol–water partition coefficient is already listed in the literature (Sangster, 1989). Volume parameter (R_K), surface area (Q_K) of group K and group interaction parameters (a_{mn}), relating to the considered systems are mentioned in Tables 1 and 2 (Gmehling *et al.*, 1982; Reid *et al.*, 1987), respectively. The estimation was made at a temperature T = 298,15 K and a mole fraction $X_{solute} = 10^{-3}$.

TABLE 1

Volume Parameter (R_K) and Surface Area (Q_K) of Group K

Compound	Group K	Number of groups K	R_K	Q_K
3-methylbenzoïc acid	$ACCH_3$	1	1,2663	0,968
	ACH	4	0,5313	0,400
	AC	1	0,3652	0,120
	COOH	1	1,3013	1,224
Di-methylbenzoïc acid	$ACCH_3$	2	1,2663	0,968
	ACH	3	0,5313	0,400
	AC	1	0,3652	0,120
	COOH	1	1,3013	1,224
n-Octanol	CH_3	1	0,9011	0,848
	CH_2	7	0,6744	0,540
	OH	1	1,0000	1,200
Water	H_2O	1	0,9200	1,400

TABLE 2

Group Interaction Parameters

	1	2	3	4
1 $ACCH_3$	0	-146,8	-146,8	603,8
2 ACH	167,0	0	0	537,4
3 AC	167,0	0	0	537,4
4 COOH	268,2	62,32	62,32	0
5 CH_3	76,50	61,13	61,13	663,5
6 CH_2	76,50	61,13	61,13	663,5
7 OH	25,82	89,60	89,60	199,0
8 H_2O	377,6	362,3	362,3	-14,09
	5	6	7	8
1 $ACCH_3$	-69,70	-69,70	803,2	5695,0

2 ACH	-11,12	-11,12	636,1	903,8
3 AC	-11,12	-11,12	636,1	903,8
4 COOH	315,3	315,3	-151,0	-66,17
5 CH_3	0	0	986,5	—
6 CH_2	0	0	986,5	—
7 OH	156,4	156,4	0	—
8 H_2O	—	—	—	0

The results obtained are consigned in Table 3:

TABLE 3

N-Octanol–Water Partition Coefficient

Solute « i »	$\gamma_i^{w,\infty}$	$\gamma_i^{o,\infty}$	$\log_{10} K_{ow}$	
			UNIFAC	Literature
3-methylbenzoïc acid	1049,6	1,3659	2,06	2,37 (Sangster,1989)
Di-methylbenzoïc acid	3600,6	1,1292	2,68	—

The examination of Table 3 reveals that the deviation between the values $(\log_{10} \mathrm{K}_{\mathrm{ow}})_{\mathrm{Uni.}}$ and $(\log_{10} \mathrm{K}_{\mathrm{ow}})_{\mathrm{Lit.}}$ of 3-methylbenzoïc acid is lower than the allowed error (0,40 on $\log_{10} \mathrm{K}_{\mathrm{ow}}$ (Sangster, 1989)). This leads us to consider that the computed value is acceptable and consequently, that UNIFAC method could be used to estimate the Octanol–Water partition coefficient. In addition, it should be known that UNIFAC is a group contribution method which does not distinguish between isomers because it uses the same group interaction parameters matrix.

CONCLUSION

The knowledge of the even approximate value (according to UNIFAC: the error is 0,31 on $\log_{10} \mathrm{K}_{\mathrm{ow}}$ and is well in the allowed interval) of the octanol–water partition coefficient represents very significant information for petrochemical industry and the environmental and pharmaceutical applications. To this end, the estimation of the octanol–water partition coefficient of the dimethylbenzoïc acid represents a contribution to the data bank.

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