Application of the UNIFAC model to represent aqueous solubility and 1-octanol/water partition coefficient for POPs

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1. Introduction

Physicochemical properties such as aqueous solubilityS_w, 1-octanol/water partition coefficient K_{ow}, and Henry's law constant H_w of POPs (persistent organic pollutants) are of importance not only for understanding their distribution behavior in the environment, but also for developing the technologies for their removal in waste treatment and from contaminated soils. The UNIFAC (UNIQUAC Functional-group Activity Coefficients) model[1], which enables to predict activity coefficient of the compound of interest in a multicomponent system, is considered to be the most appropriate and useful for estimating those properties in the case of a multicomponent system. The latest UNIFAC parameter table based on the original-type UNIFAC equation is Revision-5[2]. This UNIFAC parameter table has been modified by Kan et al.[3] to represent the physicochemical properties of PCB. Unfortunately, there is no additional modification of Revision-5 for other POPs.

In the present study, the modification of the UNIFAC parameter table Revision-5 was suggested for representing the physicochemical properties of POPs except for PCBs. In this modification, the ACCl/H_2O parameters were corrected, and then the chloroalkene (Cl(C=C))/H_2O parameters were determined from experimental S_w and K_{ow} data for POPs. The obtained parameters successfully represented physicochemical properties of POPs using the UNIFAC model. Furthermore, the UNIFAC parameter table presented here was evaluated in terms of applicability to phase equilibrium of the POPs - nonaqueous solvent systems.

2. Calculation procedure of Sw and Kow using infinite dilution activity coefficient

The UNIFAC model based on molecular thermodynamics is a group contribution method for describing activity coefficient γ_i of component i. Details for calculating γ_i are presented in the original UNIFAC model proposed by Fredenslund et al.[1]. $S_w$and K_{ow} can be estimated from the infinite dilution activity coefficient γ_i^{∞} calculated by the UNIFAC model.

For aqueous solubility S_w(mol·L^{-1}),

$$S_w = 55.56 \frac{1}{\gamma_i^{\infty}} \exp\left[-\frac{\Delta_{fus}H}{T_m R}\left(\frac{T_m}{T}-1\right)\right] = 55.56 \frac{1}{\gamma_i^{\infty}} \exp\left[-\frac{\Delta_{fus}S}{R}\left(\frac{T_m}{T}-1\right)\right] \quad (1)$$

where γ_i^{∞}, $\Delta_{fus}H$, T_m, and $\Delta_{fus}S$ denote the infinite dilution activity coefficient in water, fusion enthalpy (J ·mol^{-1}), normal melting point (K), and the entropy of fusion (J·mol^{-1}·K^{-1}), respectively.

For 1-octanol/water partition coefficient K_{ow},

$$\log K_{ow} = \log \frac{\gamma_i^{w,\infty}}{\gamma_i^{o,\infty}} + \log \frac{V^w}{V^o} = \log \frac{\gamma_i^{w,\infty}}{\gamma_i^{o,\infty}} + \log 0.151 \quad (2)$$

where the superscripts w and o indicate water and 1-octanol-rich phases, respectively. V is the molar volume (L·mol^{-}

[1]) for each phase in the 1-octanol/water binary system.

3. Method for UNIFAC parameter modification

In the correction of the interaction parameters between ACCl and H_2O groups, S_w and K_{ow} data for chlorinated benzenes (CBzs) including hexachlorobenzene, and PCDDs/DFs was used, while S_w and K_{ow} data of aldrin, dieldrin, endrin, chlordane and heptachlor was used in the determination of the Cl(C=C)/H_2O parameters.

In the collection as well as the determination of parameters, the objective function (*of*) was expressed as the sum of the deviations between experimental and calculated values with respect to logS_w and log K_{ow}.

4. Results and discussion

4.1 Correction of ACCl/H_2O interaction parameters

The calculated results in the parameter correction of CBzs and PCDDs/DFs and the comparison with those by early works[2,3] are given in Table1. The average absolute deviation AAD of log S_w and AAD of log K_{ow} for the original UNIFAC parameter table[2] were about 5.5 and 3, respectively. We can conclude that it is impossible for the original parameter values to represent S_w as well as K_{ow} even if dealing with structurally simple chlorobenzenes.

Kan's parameter table[3] was useful for PCBs only. Table 1 shows that it could not predict the S_w behavior for CBzs and PCDDs/DFs. This indicates that it is difficult to find the only pair of parameter values to quantitatively provide representation of S_w and K_{ow} for CBzs, PCBs and PCDDs/DFs.

The calculation results using the modified parameter set were in better agreement with the observed S_w and K_{ow} data than any other previous parameter tables based on Revision -5. Thus, the parameter values proposed here were the most appropriate parameter values for $a_{H2O,\ ACCl}$ and $a_{ACCl,\ H2O}$ with respect to representing the physicochemical properties of CBzs and PCDDs/DFs. However, it should be noted that this parameter set for PCDDs/DFs is more reliable for PCDDs/DFs with chlorine number higher than 3.

4.2 Determination of interaction parameters between Cl(C=C) and H_2O groups

Table 2 shows the parameter determination results for the Cl(C=C)/H_2O parameters and the deviations of log S_w and log K_{ow} between the calculated and experimental results for aldrin, dieldrin, endrin, chlordane, and heptachlor. The AADs of log S_w and log K_{ow} were 0.21 and 0.29, respectively. The modified parameter table could well represent the physicochemical properties for POPs including the chloroalkene group.

For mirex and DDT, unfortunately, the parameter table poorly represented the experimental S_w values. In contrast, the predicted results of log K_{ow} appeared to be good. From the analysis of activity coefficient in aqueous and 1-octanol phases, however, we suspected that the predicted activity coefficient in the 1-octanol phase was not reasonable.

4.3 Prediction of nonaqueous solubility

The present study examined whether or not Revision -5 was able to represent the nonaqueous solubility data of POPs. In the prediction of nonaqueous solubility, Eq. (1) was converted to Eq. (3) in order to deal with different solvents and high solubility values as follows:

$$x_i = \frac{1}{\gamma_i} \exp\left[-\frac{\Delta_{fus} H}{T_m R} \left(\frac{T_m}{T} - 1 \right) \right] \quad (3)$$

where x_i denotes mole fraction solubility.

The predicted x_i values are plotted as a function of the observed x_i values in Fig.1. The diagonal line in Fig. 1 is named as the perfect fit line, which means that the calculated values completely coincide with the experimental values. A plot close to the line indicates a good representation of the experimental value. Fig.1 shows that Revision-5 fairly represented the experimental values over six orders of magnitude except for the following two systems: 2,3,7,8-T4CDD-methanol and O8CDD -dioxane. In fact, the AAD of log x_i was 0.40. We suggest that Revision -5 of the UNIFAC parameter table is useful for predicting different nonaqueous solubilities for POPs.

References

1. Fredenslund A., Jones R.L., and Prausnitz J.M. (1975) AIChE J. 21:1086-1099.

2. Hansen H.K., Rasmussen P., Fredenslund A., Schiller M., and Gmehling J. (1991) *Ind. Eng. Chem. Res*. 30:2352-2355.

3. Kan A.T. and Tomson, M.B. (1996) *Envrion. Sci. Technol.* 30:1369-1376.

Table 1. Comparison of Calculated S_w and K_{ow} of CBzs, PCBs, and PCDDs/DFs Using Three Sets of UNIFAC H_2O/ACCl Interaction Parameters $a_{H2O,\ ACCl}$ and $a_{ACCl,\ H2O}$.

	Data point	Original Revision-5[2]	Kan's parameter[3]	This work
$a_{H2O,\ ACCl}$ / K		133.9	526.0	517.2
$a_{ACCl,\ H2O}$ / K		-274.5	92.04	2918.
ADD of log S_w				
CBzs	8	5.19	0.80	0.27
PCDDs/DFs	20	6.25	1.39	0.40
ADD of log K_{ow}				
CBzs	12	2.94	0.40	0.11
PCDDs/DFs	14	3.74	0.55	0.32

AAD: average absolute deviation.

Table 2. Calculated S_w and K_{ow} of Aldrin, Chlordane, Dieldrin, Endrin, and Heptachlor Using Newly Determined $a_{H2O,\ Cl(C=C)}$ and $a_{Cl(C=C),\ H2O}$, and Estimation Results for Mirex and DDT.

Compound	log S_w^{exp}	log S_w^{cal}	Δlog S_w	log K_{ow}^{exp}	log K_{ow}^{cal}	Δlog K_{ow}
Aldrin	-6.31	-6.31	0.00	6.5	5.87	0.63
Chlordane	-6.86	-6.86	0.00	6.0	5.84	0.16
Dieldrin	-6.29	-6.37	0.08	5.4	5.63	0.23
Endrin	-6.18	-6.99	0.80	5.2	5.63	0.43
Heptachlor	-6.32	-6.15	0.16	5.5	5.50	0.00
AAD			0.21			0.29
Determined parameters: $a_{H_2O,\ Cl(C=C)}$ = 187.6 / K, $a_{Cl(C=C),\ H_2O}$ = 2.37 / K						
Mirex	-6.81	-12.77	5.96	6.89	7.34	0.45

DDT	-7.15	-8.66	1.50	6.91	7.30	0.39

$\Delta\log S_w = |\log S_w^{exp} - \log S_w^{cal}|$, $\Delta\log K_{ow} = |\log K_{ow}^{exp} - \log K_{ow}^{cal}|$, AAD: average absolute deviation.

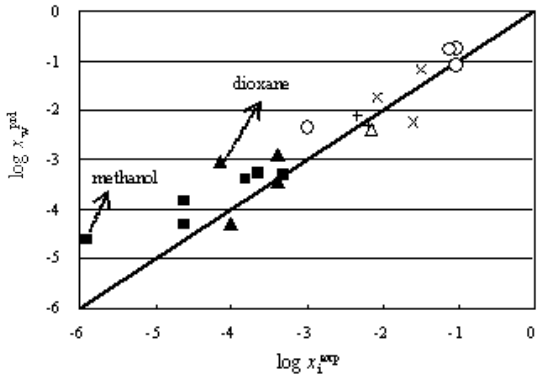

Fig. 1. UNIFAC prediction of nonaqueous solubility x_i of POPs.
log x_i^{exp}: experimental value, log x_i^{pd}: predicted value.
Symbols: ■ ;2,3,7,8-T4CDD, ▲ ;O8CDD, ○ ;dieldrin, × ;endrin
△ ;heptachlor, + ;DDT
Diagonal line: perfect fit line.